

**SYNTHETIC ASPECTS OF Cu-M-S SYSTEMS DERIVED FROM  
MS<sub>4</sub><sup>2-</sup> ANIONS ( M = Mo, W ) AND THEIR POSSIBLE  
RELEVANCE TO Cu-Mo ANTAGONISM**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
DOCTOR OF PHILOSOPHY**

**By  
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**to the  
DEPARTMENT OF CHEMISTRY [REDACTED]  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
JANUARY, 1983**

STATEMENT

I hereby declare that the matter embodied in this thesis, "Synthetic Aspects of Cu-M-S Systems Derived from  $MS_4^{2-}$  Anions (M = Mo, W) and their Possible Relevance to Copper-Molybdenum Antagonism" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



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CERTIFICATE

Certified that the work "Synthetic Aspects of Cu-M-S Systems Derived from  $MS_4^{2-}$  Anions (M = Mo, W) and their Possible Relevance to Cu-Mo Antagonism" presented in this thesis, has been carried out by Mr. Shri Bhagwat Sharan Mishra under my supervision and the same has not been submitted elsewhere for a degree.



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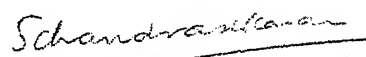
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## PREFACE

The emergence of 'Bioinorganic Chemistry' as a separate discipline of teaching and research is one of the revolutionary impacts of modern science on society. The vital role of metal ions in various biological processes is now well recognised and it is an established fact that life, at least in its present form, is not possible without active participation of these metal ions. The nutritional and toxicological effects of trace metal ions is attracting increasing attention from scientists and medical practitioners alike because many clinical significances are now attributed to the deficiency or excess of these metal ions.

The interaction of trace elements in biological systems is of vital importance in view of their stimulating and antagonistic effects on each other. Of these, the effect of excess molybdenum to deplete copper contents for metabolic circulation in ruminants, referred to as 'Cu-Mo antagonism', is supposed to be the most important interaction which relays its effect on various other stimulations and antagonisms. The tetrahedral anion  $\text{MoS}_4^{2-}$  has been proved to be the greatest antagonist of copper, so the interaction of  $\text{MoS}_4^{2-}$  with copper ions in presence of various N-donor ligands has been the objective of the thesis which may shed some light on the chemical implications of the phenomenon. Moreover, the Cu-Mo-S system is

less explored as compared to the Fe-Mo-S system which shot attention when Zumft isolated  $\text{MoS}_4^{2-}$  from nitrogenase in 1978.

Excellent instruction and good wishes of my teachers at St. Andrews, University of Gorakhpur, and IITK, a very generous attitude of the authorities of M.G. Degree College and well wishes to my colleagues therein, financial assistance from U.G.C., New Delhi in the form of Teacher Fellowship under F.I.P., ready cooperation of my friends and staff members at IITK, dedicated efforts of my late parents towards imparting the best education to their children and consistent patience, fortitude and understanding of members of my family, have contributed in respective ways towards a successful completion of the research work.

Dr. Harendra Singh, who enthusiastically encouraged me to join IITK for better training and facilities, has been responsible and instrumental for my initial training in research. His inspiring words have been a constant source of stimulation.

During my stay at IITK, I had very friendly, pleasant and gratifying association with my thesis supervisor, Professor S. Sarkar, both inside and outside the laboratory. The extent of his involvement, at every stage of development of this thesis, has been so immense that formal words of heart-felt gratitude are inadequate to express my feelings of indebtedness to him.

Hence, instead of thanking him formally in black and white,  
I am preserving the feelings in the core of my heart and  
carrying them with me for ever.

S.B.S. Mishra

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# LIST OF ABBREVIATIONS

Å	Angstrom unit, $10^{-10}$ m
$\text{cm}^{-1}$	Wave number
DMF	N,N'-Dimethylformamide
DTC	N,N'-Diethyldithiocarbamate
DMSO	Dimethylsulfoxide
$\delta$	In-plane bending or deformation
ESCA	Electron spectroscopy for chemical analysis
EXAFS	Extended X-ray absorption fine structure
eV	Electron volt
IR	Infrared
L	Ligand
M	Mo, W
M'	Metal coordinated to $\text{MS}_4^{2-}$
MCD	Magnetic circular dichroism
Me	Methyl
M.O.	Molecular orbital
nm	Nanometer, $10^{-9}$ m
$\nu$	Frequency, stretching vibration (subscripts s and as denote symmetric and asymmetric)
Ph	Phenyl
o-phen	1,10-Phenanthroline
$\gamma$ -pic	$\gamma$ -Picoline

List of abbreviations (contd.)

Py	Pyridine
R	Alkyl or aryl group
TCA	Trichloroacetic acid
UPS	Ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy

### SYNOPSIS

The thesis entitled, 'Synthetic Aspects of Cu-M-S Systems Derived from  $MS_4^{2-}$  Anions (M = Mo, W) and their Possible Relevance to Copper-Molybdenum Antagonism' has been divided into five chapters.

Chapter I presents a broad and general account of the synthetic versatility of  $MoS_4^{2-}$  and  $WS_4^{2-}$  anions as ligands. Based on these, the principal aims of current bioinorganic chemistry of  $MoS_4^{2-}$  in relation to the nitrogenase problem and Cu-Mo antagonism have been stressed upon.

Chapter II describes the scope of the present work which stemmed from the fact that little is known about the Cu-Mo-S interactions compared to Fe-Mo-S systems. Compounds containing different biometals are important but these are, in general, much more difficult to prepare. In view of these, possible synthetic approaches for different multinuclear Cu-M-S compounds have been outlined.

Chapter III describes the experimental procedures and other details involved in the present work which has been divided into seven parts. The first part 3.1 describes the methods of analysis, manipulations and characterisation of the newly prepared compounds. Part 3.2 describes the synthesis of binuclear species of the general formula  $[NCSCuMS_4]^{2-}$  and



$[(o\text{-phen})\text{CuMS}_4]^-$ . Part 3.3 deals with the synthesis of symmetric trinuclear species of the type  $[(o\text{-phen})\text{CuS}_2\text{MS}_2\text{Cu}(o\text{-phen})]$ . When  $\text{Mo}_2\text{S}_2^{2-}$  were used compounds of the type  $[(\text{phen})_2\text{Cu}_2\text{Mo}_2\text{S}_2]$  were isolated. The use of triphenylarsine as coligand resulted the complexes of the composition  $[(\text{AsPh}_3)_3\text{Cu}_2\text{MS}_4]$ . Part 3.4 describes the preparation of tetranuclear compounds having the general formula  $[(\text{AsPh}_3)_3\text{Cu}_3\text{MS}_3\text{X}]$  ( $\text{X} = \text{S}, \text{O}$ ). Part 3.5 describes the preparation of pentanuclear species of the composition  $[\text{L}_4\text{Cu}_4\text{X}_2\text{MS}_4]$  ( $\text{L} = \text{py}, \gamma\text{-pic}$ ;  $\text{X}^- = \text{SCN}^-, \text{Cl}^-$ ). Part 3.6 describes the general properties of all the polynuclear complexes synthesized. The last part (3.7) deals with the interaction of freshly precipitated cupric sulphide with generated  $\text{MoS}_4^{2-}$  in aqueous medium wherein it has been shown that aqueous thiomolybdate can solubilise  $\text{CuS}$  with concomitant reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$  with the formation of a soluble species from which complexes of the type described in part 3.3 and 3.5 can be isolated using the appropriate stoichiometry and ligand. A possible role of this reaction to  $\text{Cu-Mo-S}$  interaction in  $\text{Cu-Mo}$  antagonism is stressed upon.

Chapter IV describes the physico-chemical and structural investigations of the synthesized compounds described in the preceding chapter. The studies include electronic, IR, Raman, resonance Raman and X-ray photoelectron spectroscopy and X-ray powder diffraction patterns. Emphasis has been made to understand the perturbation caused by complexation of closed shell

Cu(I) on the ligand internal transitions of the  $MS_4^{2-}$  chromophore. Resonance Raman spectroscopy has been utilized to determine unambiguously the structure of the symmetrically coordinated trinuclear complex (described in part 3.3) for which suitable single crystals for a crystal structure determination could not be obtained. The outcome of these studies conform with the  $d^{10}(\text{Cu}) \rightarrow MoS_4^{2-}$  interaction. The genesis of these heteropolynuclear species has been correlated with the polynuclear Cu(I) complexes of different geometry.

Chapter V presents the chemical implications of Cu-Mo antagonism. On the line of recent observation that the formation of a copper-thiomolybdate-protein complex makes the copper unavailable for metabolic purposes, our results of the present investigation are discussed. The sequential interaction between  $Cu(II)/MoO_4^{2-}/H_2O$  and  $H_2S/S^{2-}$  is stressed upon and the utilization of N-donor ligands in these systems has been made to account for protein interactions with Cu-Mo-S systems. The use of N-donor ligands in isolating several Cu-Mo-S species may serve as a model for such interactions.

## CHAPTER I

### INTRODUCTION

Thiometallates of Mo(VI) and W(VI) are known since 1826 when Berzelius synthesised the ions  $\text{MoS}_4^{2-}$  and  $\text{WS}_4^{2-}$  [1]. Although the mixed oxothioanions  $[\text{MO}_{4-n}\text{S}_n]^{2-}$  (M = Mo, W) have been described in older literature [1] only the preparations of the salts of  $\text{MS}_4^{2-}$  could be reproduced [2] using the reported methodology.

Though molybdenum can exist in several oxidation states, yet in binary sulphur compounds only  $\text{MoS}_2$  (which exists also in natural molybdenite),  $\text{Mo}_2\text{S}_3$  and  $\text{MoS}_3$  are known [3]. Sulphur can replace oxygen in several oxo-compounds of molybdenum but the substituted molybdenum-sulphur compounds differ entirely in structure, properties and composition [4,5].

Molybdates (VI) and tungstates (VI) form a class of compounds by polymerisation which are known as heteropoly and isopoly compounds whereas the solution behaviour of thiomolybdate and thiotungstate species is different from that of the corresponding oxygen analogues.

The reactivities of these thiometallates and their applications in complex chemistry have been systematically explored only recently. Thus the first complex chemistry of these anions has been reported by isolating the salt of the bis(tetrathio-tungstato)nickelate(II) anion  $[\text{Ni}(\text{WS}_4)_2]^{2-}$  [6]. This is the first discrete inorganic complex anion wherein the centrally located hetero ion nickel(II) is complexed with two tetrathio-metallate anions through sulphur. The isolation of this type of discrete thioheteroanions essentially requires the use of bulky cations like tetraphenylphosphonium or tetraphenylarsonium ions. The corresponding thiomolybdate complex could also be prepared; however, the reaction appears to be not so clean and the precipitation of some polymeric species possibly mixed with makes recrystallisation essential to isolate the pure product [7]. This polymerisation tendency for certain metal ions on reaction with thiometallate is known and one example of this type of species is  $\text{NH}_4\text{CuMoS}_4$  [8].

With the success in isolating the nickel complexes Müller and coworkers systematically exploited the ligational behaviour of these thiometallate anions [9]. Thus the complexes of the

general formula  $[M'(MS_4)_2]^{2-}$  ( $M' = \text{Zn}$  [10],  $\text{Fe}$  [11],  $\text{Co}$  [12,13],  $\text{Pd}$  [14],  $\text{Pt}$  [14],  $\text{Cd}$  [15] and  $M = \text{Mo}$  or  $\text{W}$ ) were synthesized. In isolating this series of complexes the difficulty associated with polymerisation tendency has been encountered when  $\text{MoS}_4^{2-}$  is used as ligand.

The other oxothiometallate systems of  $[\text{Mo}_{4-n}\text{S}_n]^{2-}$  series have also been tried and with the exception of  $[\text{Mo}_3\text{S}]^{2-}$ , whose isolation in pure form is difficult, all form similar type of complexes [16-21].

The characterisation of these complexes have been done mostly by vibrational spectroscopy followed by other physico-chemical methods and finally by X-ray structural determination. Some of the properties of these complexes are summarised in Table 1.1.

Depending on the demand of the central metal atom present in these complexes, square planar and tetrahedral geometry of the central atom is achieved (Figure 1.1a, 1.1b). The first octahedral arrangement of central metal has been reported when a similar reaction is carried out using tin [16]. The structure of this polynuclear species,  $(\text{PPh}_4)_4[\text{Sn}_2(\text{WS}_4)_4]$  has been shown in Figure 1.1c.

The above stated tin complex suggested the possibility of the utilisation of these thiometallate ions with varied coordination ability. In bis(thiometallato) complexes, the reactivity of the central metal has been first studied with the iron and

TABLE 1.1

COMPLEXES OF THE TYPE  $[M'(MO_{4-n}S_n)_2]^{n-}$  AND THEIR PROPERTIES

Anion	Colour	NIR/UV/VIS $[10^3 \text{ cm}^{-1}]$			IR $[\text{cm}^{-1}]$			Reference
		L-d(M')	L-L*	d-d	$\nu(\text{MO}_{\text{term}})$	$\nu(\text{MS}_{\text{term}})$	$\nu(\text{MS}_{\text{br}})$	
1	2	3	4	5	6	7	8	9
$[\text{Fe}(\text{MoS}_4)_2]^{3-}$	Violet	15.9	19.7, 24.4	-	-	495, 472	438	19, 20
$[\text{Ni}(\text{MoS}_4)_2]^{2-}$	Dark brown	-	19.5, 25.3, 30.0	-	-	513, 494	455.5, 442.5	10
$[\text{Pd}(\text{MoS}_4)_2]^{2-}$	Red	-	21.2, 26.1, 28.6, 31.6	-	-	513, 497	450, 435	14
$[\text{Pt}(\text{MoS}_4)_2]^{2-}$	Red	-	19.5, 24.3, 27.5, 32.5	-	-	510, 496	454, 433	14
$[\text{Zn}(\text{MoS}_4)_2]^{2-}$	Brown	-	17.5, 21.4, 31.9, 40.5, 42.9	-	-	516, 499	456, 434	10
$[\text{Ni}(\text{MoOS}_3)_2]^{2-}$	Brown	-	21.8, 27.6, 31.0	-	896, 884	500, 492	458, 446	21
$[\text{Zn}(\text{MoOS}_3)_2]^{2-}$	Orange	-	21.7, 25.1, 33.0	-	898	502	456, 437	21
$[\text{Co}(\text{MoO}_2\text{S}_2)_2]^{2-}$	Green	14.7	29.1, 33.1	8.3	903, 884	-	453, 447	21

...contd.

Table 1 (contd.)

1	2	3	4	5	6	7	8	9
$[\text{Ni}(\text{MoO}_2\text{S}_2)_2]^{2-}$	Brown	-	27.0, 31.0, 34.7	14.3	896, 880	-	463, 453	139
$[\text{Fe}(\text{WS}_4)_2]^{3-}$	Orange	18.0	23.27	-	-	493, 484	438	11, 21
$[\text{Fe}(\text{WS}_4)_2]^{2-}$	Green	16.2	23.4, 26.7	8.7	-	493, 484	438	11
$[\text{Co}(\text{WS}_4)_2]^{2-}$	Olive green	12.2	25.8	8.6	-	500, 491	450, 442	6, 12, 13
$[\text{Ni}(\text{WS}_4)_2]^{2-}$	Red-brown	-	23.8, 26.3	14.3	-	496, 490	499	6, 12
$[\text{Pd}(\text{WS}_4)_2]^{2-}$	Brown-red	-	25.2, 27.2, 31.9	-	-	499, 491	440	14
$[\text{Pt}(\text{WS}_4)_2]^{2-}$	Brown orange	-	24, 32.0	-	-	498, 489	446, 438	21
$[\text{Zn}(\text{WS}_4)_2]^{2-}$	Orange	-	21.7, 25.3	-	-	492.4, 487.2	445.5, 435	6, 12
$[\text{Cd}(\text{WS}_4)_2]^{2-}$	Orange	-	21.6, 25.3	-	-	493, 486	435	15
$[\text{Co}(\text{WOS}_3)_2]^{2-}$	Olive green	13.8	27.2, 30.3	8.3	917, 907	490, 485	445	6, 12
$[\text{Ni}(\text{WOS}_3)_2]^{2-}$	Brown	-	26.3, 30.1	14.5	921, 908	496, 486	450	6, 12
$[\text{Zn}(\text{WOS}_3)_2]^{2-}$	Yellow	-	25.3, 29.5	-	918, 904	495, 485	440	6, 12
$[\text{Co}(\text{WO}_2\text{S}_2)_2]^{2-}$	Blue green	16.4	31.7	7.5	927, 892	-	440	21
$[\text{Ni}(\text{WO}_2\text{S}_2)_2]^{2-}$	Brown-yellow	-	31.5, 34.7	15.0	916.1, 882.4	-	451.1	21

cobalt systems. It has been shown that the cobalt or iron, when tetrahedrally complexed with the thiometallate groups can enhance their coordination number and facile nitrosylation is possible on these systems to isolate species of the type  $[M'(NO)(WS_4)_2]^{2-}$  [11]. Interestingly, the starting iron complex,  $(PPh_4)_2[Fe(WS_4)_2]$  when tried to recrystallise in DMF, changes its colour from green to red-brown leading thereby to the isolation of  $(PPh_4)_2[Fe(DMF)_2(WS_4)_2]$  [15, 17]. Thus, the tendency of iron in these complexes to enhance its coordination number has been demonstrated. These features in iron complex are interesting in the sense that essentially it contains the heteroatoms which are present in nitrogenase. The evidence for the possible involvement of  $MoS_4^{2-}$  anion as structural component of nitrogenase active site was shown by Zumft [18] by chromatographic separation of  $MoS_4^{2-}$  from acid treated reneutralized solution of Fe-Mo protein from Clostridium pasteurianum which resulted in a new thrust on the investigation of  $Fe^{2+}/MoS_4^{2-}$  system. The synthetic methodology since then changed from aqueous to non-aqueous medium with the direct involvement of tetraalkyl ammonium tetrathiomolybdate and iron complexes for solubility reasons. Thus when iron xanthate [19] or iron dithiocarbamate [20] complexes are used, complex of the type  $[Fe(MoS_4)_2]^{3-}$  could be isolated. In both these reactions, the formal reduction of the central iron, which was erroneously thought as the reduction of molybdenum, has occurred with the proposition that the thioligands serve as reducing agents [19, 20].



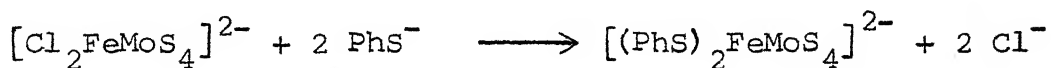
The previous attempt [11] to isolate  $[\text{Fe}(\text{MoS}_4)_2]^{2-}$  by analogy to corresponding tungsten analogue leads to the isolation of a polymeric amorphous compound of approximate composition  $(\text{PPh}_4)_2[\text{Fe}(\text{MoS}_4)_2]$ . However, the Mössbauer spectrum of the frozen solution containing  $\text{Fe}^{2+}/\text{MoS}_4^{2-}/\text{H}_2\text{O}$  shows the presence of  $[\text{Fe}(\text{MoS}_4)_2]^{3-}$  anion [21]. The electronic spectrum also suggests the existence of this species containing  $\text{MoS}_4^{2-}$  in equilibrium. These findings are interesting which demonstrate that sulphur containing ligands are not necessary for the reduction and  $\text{MoS}_4^{2-}$  itself can serve the same purpose. As stated earlier, the reaction between  $\text{MoS}_4^{2-}$  and other metal ions in aqueous medium always leads to some polymerisation which could be avoided by appropriate choice of the solvent. 1:1 acetonitrile:water has been found to be the most effective to prevent this polymerisation step. Another point in isolating these anionic species is the proper choice of the bulky cationic group. Thus, it is possible to isolate the  $[\text{Fe}(\text{MoS}_4)_2]^{3-}$  ion as tetraalkyl ammonium salt from a solution of  $(\text{NH}_4)_2\text{MoS}_4$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1). The mechanism for the reduction of the central metal has not been clarified. The reduction can be facilitated by taking an other iron salt. Thus a suspension of  $[\text{Fe}(\text{C}_2\text{O}_4)]$  in DMF reacts slowly but smoothly with  $\text{MoS}_4^{2-}$  to generate the reduced species [21].

So far, the ligational behaviour of thiometallate ions rests mainly on their ability to function as bidentate ligand. The only exception to this behaviour has been noticed for the tin complex where it can function as a tridentate ligand. In the

polymeric  $\text{NH}_4\text{CuMoS}_4$ , the coordination ability is increased demonstrating its nature as a four-fold coordinating ligand. For the synthetic chemist, thus, the following facts become interesting:

- i) To understand the ligational behaviour of  $\text{MS}_4^{2-}$  ion.
- ii) Variation of the iron compounds to know the metathetical dependence of the reaction.
- iii) The possible involvement of any redox reaction.
- iv) The choice of appropriate cation to stabilize the species formed.

When ferrous chloride has been used as iron source in pure anhydrous solvent, the 1:1 complex anion  $[\text{Cl}_2\text{FeMoS}_4]^{2-}$  is formed which could be isolated by the use of tetraalkylammonium [22], mixed tetraalkylammonium tetraphenylphosphonium [23,24] and tetraphenylphosphonium cations [25]. In this complex anion the Fe-Cl bond is fairly covalent in nature. However, with thiophenolate anion the following metathetical reaction takes place [22]:



The same complex anion can be directly obtained by reacting  $\text{MoS}_4^{2-}$  with  $[\text{Fe}(\text{SPh})_4]^{2-}$  [26]. Thus a complete environment of sulphur around iron attached to thiomolybdate is possible. Similar reaction can be expanded by reacting  $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$  with organic trisulphide whereby complex of the type  $[(\text{S}_5)\text{FeMoS}_4]^{2-}$

containing the novel  $S_5^{2-}$  ligand is formed [27].

From the nitrogenase point of view, Shah and Brill isolated an Fe-Mo cofactor from the Fe-Mo component protein of nitrogenase [28]. The analytical ratio between Fe:Mo:acid labile sulphide has been reported to be 8:1:4 to 6 respectively. Molybdenum K-edge X-ray absorption fine structure (EXAFS) analyses of the Mo-Fe protein and MoFe-co reveal that in all samples the short range order around the molybdenum should be very similar. From these studies, the two possible models inferred with the occupancy of the first and second coordination shells around the molybdenum atom are shown in Figure 1.2 [29,30].

So far, in the material discussed above regarding Fe-S-Mo chemistry, two units have been made with Fe:Mo ratio to be 1:1 and 1:2. Guided by the nitrogenase Mo EXAFS results, systematic investigations have been intensified to synthesise compounds with the closest approach to the above referred models. Coucouvanis and coworkers using a complicated reaction between  $[(PhS)_2FeMoS_4]^{2-}$  and  $FeCl_3$  synthesised the anionic species  $[(Cl_2Fe)_2MoS_4]^{2-}$  [26]. In this trinuclear complex,  $MoS_4^{2-}$  acts as a doubly bridging ligand. By a simplified reaction procedure using  $FeCl_2$  and  $MoS_4^{2-}$ , the same complex could be isolated in quantitative yield [25].

This compound may be thought to be the closest approach to the trinuclear model (Figure 1.2a). The enhancement of the coordination number of central molybdenum from four to five would have

been a better approach which one could meet only by the reduction of the central molybdenum. The exchange of chloride attached to iron by thiolate group, as has been done with the dinuclear species, (1Fe, 1Mo), would be interesting where the trimetallic core would be ligated through only sulphur donors.

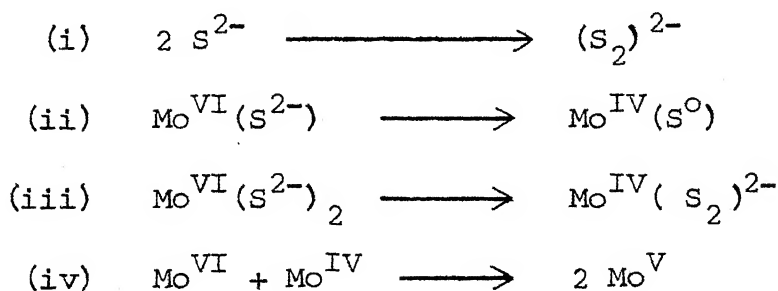
Attempt has been made to enhance the coordination number of the central molybdenum attached to iron. Thus, reaction between  $\text{Cs}_2\text{MoOS}_3$  and  $\text{FeCl}_2$  in presence of sulphur leads to the formation of the complex  $[\text{Cl}_2\text{FeMoOS}(\text{S}_2)]^{2-}$  whose structure is shown in Figure 1.3 [31]. The formation of the molybdenum species definitely follows through a complicated reaction sequence. However, this could show, at least, that molybdenum can exist in pentacoordination though the formal oxidation state of this is six. Attachment of another iron unit through the  $\text{S}_2^{2-}$  group would be interesting provided a cleavage mechanism to cleave S-S bond is developed. Attempts to attach iron without cleavage of this bond failed and similar reaction using  $\text{MoS}_4^{2-}$  instead of  $\text{MoOS}_3^{2-}$  does not give the analogous sulphur compound [32].

The influence of elemental sulphur or polysulphide ion on  $\text{MoS}_4^{2-}$  alone or  $\text{MoS}_4^{2-}$  and iron resulted in some interesting reactive chemistry which is quite relevant to understand the role of molybdenum in the nitrogenase and in other biosystems.

### Thiomolybdate/elemental S/polysulphide ion Systems

Another aspect of molybdenum sulphur chemistry lies in the formation of sulphur rich polythiomolybdates. Molybdenum exists in several oxidation states in this series of compounds witnessing the high affinity of molybdenum for sulphur and for polysulphide ions like  $S_2^{2-}$  and  $S_4^{2-}$ .

There is no analogy for the condensed thiomolybdate comparable to those of oxomolybdate. The condensation reactions subsequent to protonation of thiometallate ions occur at a lower pH compared to those of the oxoanions because of the fact that the proton affinity of sulphur is appreciably lower than that of oxygen. For the thiometallate system the condensation behaviour is more complex in nature where intramolecular redox processes may take place alongwith a condensation reaction. In near neutral aqueous solution decomposition of the species takes place which proceeds with the condensation steps. A probable involvement of these reactions occurring simultaneously can be of the following type:



The first sulphur rich molybdenum compound of this type is

$[\text{Mo}_2\text{S}_{12}]^{2-}$  which could be isolated by the reaction between molybdate and polysulphide ion [33-35].

By following a roughly similar experimental condition but at an elevated temperature, the discrete metal sulphur cluster,  $[\text{Mo}_3\text{S}_{13}]^{2-}$ , could be isolated [36,37]. It is interesting to note that the directed synthesis of cluster compounds is problematic in transition metal chemistry [38]. For molybdenum and tungsten with  $d^n$  configuration, cluster types are expected to be dumb-bell shaped ( $n = 1$ ), triangular ( $n = 2$ ), tetrahedral ( $n = 3$ ), and octahedral ( $n = 4$ ). Thus, the dimeric  $[\text{Mo}_2\text{S}_{12}]^{2-}$  represents the first species of this series and the trimeric  $[\text{Mo}_3\text{S}_{13}]^{2-}$  represents the second species of this series. Due to the high charge concentration for the ions containing  $n = 3$  and  $n = 4$ , difficulties are expected in isolating these species using sulphur as ligand source. However, the so called  $\text{MoCl}_2$  has got octahedral  $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$  arrangement and the frame work satisfies  $n = 4$  condition. The missing  $n = 3$  system could now be isolated using  $\text{Mo}_4\text{S}_4$  cubane core in the compound  $[\text{Mo}_4\text{S}_4(\text{CN})_{12}]^{8-}$  [39].

By the reaction of thiomolybdate or molybdate/ $\text{S}^{2-}$  system with reducing nitrosylating agent  $\text{NH}_2\text{OH}$ , remarkable polynuclear complexes of the type  $[\text{Mo}_4(\text{NO})_4\text{S}_{13}]^{4-}$  [40;41] and  $[\text{Mo}_4(\text{NO})_4\text{S}_{12}\text{O}]^{2-}$  [42] could be isolated. In all the above referred polynuclear molybdenum-sulphur systems  $\text{S}_2^{2-}$  group is present and its mode of attachment varies from compound to compound suggesting the

versatile nature of this ligand. The structural units of these compounds are reproduced in Figure 1.4.

The isolation and reactivity of these compounds are significant for problems in the bioinorganic field [43-45] and in connection with the evolution of primitive molybdenum enzymes [46,47].

The reactivity of thiomolybdate with elemental sulphur has been explored leading thereby to sulphur ring compounds attached to molybdenum with concomitant reduction of molybdenum. Thus,  $\text{MoS}_4^{2-}$  with elemental sulphur or with organic trisulphide leads to the formation of a special class of compounds like  $[\text{MoS}(\text{S}_4)_2]^{2-}$  wherein the formal oxidation state of molybdenum is +4 [48]. The corresponding complex  $[\text{MoO}(\text{S}_4)_2]^{2-}$  is also known [49]. From the same reaction mixture, on longer keeping, dimeric asymmetric complex containing both  $(\text{S}_2)^{2-}$  and  $(\text{S}_4)^{2-}$  groups like  $[(\text{S}_2)\text{MoS}_2\text{Mo}(\text{S}_4)]^{2-}$  could be obtained [50]. The same species could be obtained by the reaction of  $[\text{Mo}_2\text{S}_{12}]^{2-}$  and thiolate [51]. However, symmetric oxo-species like  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_4)_2]^{2-}$  and  $[\text{Mo}_2\text{O}_2(\text{S}_2)_2]^{2-}$  could be obtained when  $[\text{MoOS}_3]^{2-}$  is used instead of  $\text{MoS}_4^{2-}$  [52,53].

Once again the tungsten-sulphur chemistry is not parallel to molybdenum-sulphur system as discussed above. However, acidification of aqueous  $\text{WS}_4^{2-}$  leads to the formation of  $[(\text{HS})\text{WS}_3]^-$  [54], which on keeping produces mixed valence species like  $[\text{W}_3\text{OS}_8(\text{H}_2\text{O})]^{2-}$  or  $[\text{W}_3\text{OS}_8]^{2-}$  [55]. The pure sulphur analogue  $[\text{W}_3\text{S}_9]^{2-}$

could be isolated in non-aqueous medium in which the hydrolysis of the species is prevented. The next higher homologue  $[W_4S_{12}]^{2-}$  has also been isolated [21].

#### Thiomolybdate/ $Fe^{3+}/S^O$ /thiolate System

A systematic investigation on the "Spontaneous Self-Assembly" of Fe/S/thiolate systems to generate cluster species similar to Fe-S proteins resulted in a reasonably satisfactory picture of the modes of self-assembly of these clusters [56,57]. Two independent groups simultaneously carried out one of the most important synthetic approaches utilizing this self-assembly behaviour of iron thiolate system with tetrathiomolybdate [58-61]. This new family of clusters commonly called as double cubane type (Figure 1.5) essentially comprised the desired  $MoFe_3S_4$  unit which is a structural proposal for the molybdenum site in nitrogenase (see Figures 1.2a and 1.2b) (vide supra).

Unfortunately molybdenum in these species is present in bridged fashion with no room to activate molecular nitrogen in nitrogenase if one thinks, the binding site of molecular nitrogen to molybdenum, a possibility. Thus cleavage of the double cubane is essential to have a nearer approach to one of the models deduced from EXAFS analyses. Holm and coworkers using a series of judicious experimental manipulations were able literally to cleave this double cubane cluster and the species resulted by doing so are presented in Figure 1.6 [62].



However, all the model compounds synthesised so far do not carry the full complement of iron as has been shown by the chemical analysis of FeMo-co. As pointed out by Holm [63], the incorporation of  $\text{MoFe}_3\text{S}_3$  fragment of a  $\text{MoFe}_3\text{S}_4$  cluster into a larger cluster comprising iron and sulphur to meet the necessary stoichiometry as indicated by the chemical analysis of FeMo-co would be the most appropriate model for the nitrogenase.

#### Thiomolybdate/Copper and other coinage metal systems

The ligational behaviour of thiometallates with coinage metal systems had not been studied in great detail until recently. This was partly due to the polymeric nature of the species formed where structural characterisation had been difficult in view of their insoluble nature which place them sufficiently inert for most of the chemical reactions. The first structurally characterised species of this class is the polymeric  $\text{NH}_4\text{CuMoS}_4$  [8]. One of the most important aspects of this type of reaction is the involvement of reduction of cupric ion to cuprous, in presence of thiometallate anions. The many-fold functions of the thiometallate ions regarding their ligational behaviour have been aptly exploited using closed shell metal ions. The methodology used in these synthetic approaches is to use the suitable coligand which can terminate the inherent polymerisation tendency by blocking the extracoordinating sites. However, the higher congeners of this group of metals, especially gold, interacts with

the thiometallate systems without the use of any coligand to produce discrete anions like  $[\text{Au}_2(\text{WS}_4)_2]^{2-}$  leading thereby to an interesting ring structure [64]. Essentially this anion consists of two Au atoms bridged by two  $\text{WS}_4^{2-}$  groups in bidentate fashion leaving two W=S terminal sulphurs out of the ring. The corresponding thiomolybdate compound could not be prepared, which is also true for the case of the tin compound described earlier.

Besides synthetic, structural and bonding type of these species another important aspect emerges on the possible role of thiomolybdate to interact with copper causing the depletion of copper in metabolism. The significance of thiomolybdate in this type of bioinorganic problem, that is, Cu-Mo antagonism arose considerable interest to explore the versatile coordination behaviour of thiomolybdate with copper.

The complex chemistry of Cu(I) is very much complicated and the stoichiometries of these compounds furnish little clue to their structures. Cu(I) can form mononuclear, binuclear and polynuclear compounds wherein its coordination number ranges from 2 to 4 [66,67]. In the polynuclear variety, assembly of tetranuclear, pentanuclear, hexanuclear, octa- and decanuclear aggregates are known besides the long known chain structural type [68]. It is noteworthy that the selective choice of sulphur or phosphorous donor ligand is an important feature for the stabilization of the polynuclear species. In binuclear compounds halogen bridge structure is predominant with phosphorus

donor ligands whereas in the chain structure chloride and cyanide are used to form bridges. Thus, the structure of complex depends on the nature of the ligands.

Both symmetrical and unsymmetrical (Figure 1.7) structural type of binuclear species with the compositions  $\text{Cu}_2\text{X}_2\text{L}_4$  and  $\text{Cu}_2\text{X}_2\text{L}_3$ , respectively are known. The steric bulk of the ligand can influence to force a structural variety over the other, and an example to this variation can be shown in Figures 1.7c & 1.7d for complexes of the composition  $(\text{CuXL})_4$  (X = halogen, L = tertiary phosphine, pyridine) [69,70]. In all the above stated pure copper complexes the occupancy of copper is either tetrahedral or trigonal in nature.

These inherent structural units of pure copper complexes are still retained when Cu(I) forms polynuclear complexes with thiometallates. Thus tetrathiomolybdate can replace halogen bridges from structures presented in Figure 1.7b to give species like  $[(\text{PR}_3)_3\text{Cu}_2\text{MoS}_4]$  [23]. However, the symmetrical structural variety (Figure 1.7a) could be obtained only when copper is substituted by silver [21]. The stoichiometry of the tertiary phosphine used dictates the structural features of the silver compounds. The unsymmetrical variety for this is also known [21]. As stressed on the necessity of the bulkiness of the ligand it is evident that the sizes of the metal play a necessary role in deciding the geometry. For silver, the existence of both the varieties do suggest a limiting borderline case for silver which

is reflected even in some pure Ag(I) complexes. Thus, the complex  $(\text{Ag}^{\text{I}}\text{PPh}_3)_4$  analogous to  $(\text{CuXL})_4$  can be isolated in both stereoisomeric forms (Figures 1.7c & 1.7d). However, the chair form is most stable [71,72].

The exploration of Cu-Mo-S system reveals the structural features of the pure copper compounds. Thus, the cubane structural variety (Figure 1.7c) could be obtained in the heteropoly-nuclear complex,  $[\text{Cu}_3\text{MoS}_3\text{Cl}(\text{PPh}_3)_3\text{S}][73]$ . This structural unit may be thought of being formed by substitution of the  $\{\text{X}_3\text{CuL}\}^{2-}$  fragment in the cube by the  $\{\text{S}_3\text{MoS}\}^{2-}$  unit. Generation of this heterocube is almost identical to the parent homocubane variety where all the constituent atoms used for cubane structure retain their coordination number. However, this distorted cube can adopt another chair like structure, and for the corresponding silver complex it has been shown to be the most stable form. The chair form comprising  $\text{M}_4\text{X}_4$  core contains three and four coordinate metal and two and three coordinate X in pairs, respectively. Recently a complex of the composition  $(\text{PPh}_4)_2[(\text{CuCl})_3\text{MoS}_4][74]$  has been isolated and its structure resembles that of the chair form where it may be thought that a unit of  $\{\text{LCuX}_3\}$  from base of the chair form and one  $\{\text{X}^-\}$  from the bottom edge of it have been replaced by a  $\text{MoS}_4$  unit. The resultant hetero complex resembles the parent core where the only difference lies in the reduction of a pair of two coordinate halogen bridges by one two-coordinate sulphur bridge in the heterosystem and an

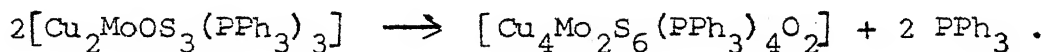
increase of one more three coordinate sulphur bridge. This apparent change in the number and coordination number of halogen and sulphur bridges in the two structures results due to replacement of  $\text{CuX}_3$  and X from the parent compound by  $\text{MoS}_4^{2-}$  unit. The missing link in  $\text{CuX}_3$  and X exists already in the substituent  $\text{MoS}_4^{2-}$  where all the four bridging sulphurs are primarily attached to molybdenum. The structure of this hetero species is shown in Figure 1.8.

Thus, it is evident that the polymerisation process which is inherent in Cu-Mo-S system, especially in protic medium, can be checked by blocking the coordination sites of copper using suitable donor ligands. The synthetic approach to isolate the above stated species mostly lies in the use of cupric ion as the source of copper. The cupric ion in presence of reducing phosphine and thiometallate environment changes to cuprous which can be smoothly incorporated with the thiometallate unit in situ. However, the polymeric chain unit of cuprous compound can be cleaved to get the discrete compound. The use of this methodology sometimes reflects the dependence of such reactions with other factors. Thus when the polymeric CuCN is allowed to interact with  $(\text{PPh}_4)_2\text{MoS}_4$ , discrete dinuclear  $(\text{PPh}_4)_2[\text{NCCuMoS}_4]$  could be obtained whereas when  $(\text{NMe}_4)_2\text{MoS}_4$  is used as a source of  $\text{MoS}_4^{2-}$ , the polymeric unit comprising  $[\text{NCCuMoS}_4]^{2-}$  is formed which is coordinated to the copper atoms of an infinite CuCN chain [75].

The tungsten analogues of the above mentioned complexes are also known and in the cubane type of compound the radially oriented molybdenum-sulphur could be replaced by molybdenum-oxygen when  $\text{MoS}_3^{2-}$  was used instead of  $\text{MS}_4^{2-}$ .

Another type of cage structure of the composition  $[\text{Cu}_4\text{W}_2\text{S}_6(\text{PPh}_3)_4\text{O}_2]$  [76] could be obtained using an identical procedure as applied for the synthesis of the cube compound. However, the corresponding molybdenum analogue could not be isolated but when silver is used instead of copper, the cage compound of molybdenum is readily formed. This type of structural variety should have some resemblance to hexanuclear pure copper complexes. Unfortunately only hydride species is structurally characterised [77] which has got no resemblance to these heteronuclear cage species.

Recently the copper-molybdenum cage compound has been isolated by use of the intermediate compound having the core  $\{\text{Cu}_2\text{MoOS}_3(\text{PPh}_3)\}$  containing a tricoordinate  $\{\text{Ph}_3\text{PCuS}_2\}$  unit and one tetracoordinate  $\{(\text{Ph}_3\text{P})_2\text{CuS}_2\}$  unit [78]. This can be dimerised in solution with the expulsion of  $\text{PPh}_3$  to generate the cage unit as



### Spectroscopic Investigations and Chemical Bonding in Thiometallate Complexes

#### 1. Electronic Structure and Stability

The strong metal ligand interactions involved in these complexes containing thiometallates with unusual electronic

properties are important in relevance to their application in bioinorganic field. This fact can be demonstrated by the use of various physical measurements which also lead to the elucidation of the molecular structure. Electronic spectroscopy of thio-metallate complexes particularly with metals containing open d-shell shows the involvement of delocalised molecular orbitals characteristic of strong interaction between the central metal and thiometallate ligand.

The simplified molecular orbital scheme for  $MS_4^{n-}$  ion with  $T_d$  symmetry (Figure 1.9) suggests the involvement of  $\pi$  bonds which is also demonstrated by various other physical measurements. The proportion of  $\pi$  contribution to the respective metal-sulphur bond of analogous species increases in the sequence  $V < Mo < W < Re$ . However, this range of  $\pi$  contribution is appreciably higher compared to thioanions of the main group elements [79]. Unambiguous assignment is only possible for the longest wavelength band, that is,  $t_1 \rightarrow 2e(\nu_1)$  using MCD measurements [80,81]. Assignments to the higher energy transitions ( $\nu_2$  and  $\nu_3$ ) are not straightforward. Investigations on the influence of various coordination centres to these bands of  $MoS_4^{2-}$  and some empirical considerations suggest that  $\nu_2$  and  $\nu_3$  bands may be roughly assigned to the transitions  $3t_2 \rightarrow e$  and  $t_1 \rightarrow 4t_2$ , respectively [80].

The known complexes of the type  $[M'(MS_4)_2]^{2-}$  show characteristic absorption bands whose positions are only roughly

comparable to those in free thiometallates. The  $S \rightarrow M$  transition in these complexes is split due to the lowering of local symmetry about the central atom of the  $MS_4^{2-}$  unit. Because of the strong  $M' \rightarrow L$  interaction, the spectra in the region of ligand internal transitions depend markedly on the nature of the central atom. Thus, there is a characteristic splitting of the  $\nu_1$  band of  $WS_4^{2-}$  in the nickel complex. In contrast, the longest wavelength band in the corresponding thiomolybdate analogue is strongly shifted in the direction of longer wavelength (Table 1.1).

This large shift towards longer wavelength suggests strong  $d\pi(Ni)$  interaction with the ligand orbitals in  $[Ni(MoS_4)_2]^{2-}$ . This interaction is so strong that a formulation of this compound as a  $Ni^{II}-Mo^{VI}$  complex can not be said accurately. Cyclic voltametric studies lend support to this charge delocalisation with the facile stepwise redox behaviour of this type of species [82]. The corresponding iron and cobalt complexes of the above type show a remarkable band of high intensity in the NIR/VIS region (Table 1.1). The instability of the  $[Fe(MoS_4)_2]^{2-}$  ion can also be explained using a qualitative molecular orbital scheme as shown in Figure 1.10. Since the  $3d(M')$  level is at an energy comparable to  $t_1$  of the free  $MoS_4^{2-}$  there is a remarkable  $M'-L \sigma$  interaction.

It has been suggested that when  $M'-M$  separation is of the order of  $2.8 \text{ \AA}$  direct metal-metal interaction is also possible [21].



The salient features of this m.o. description suggest the following:

- (i) In these trinuclear complexes the electron density on the M' centre is diminished while that on the M centre is increased relative to free  $\text{MS}_4^{2-}$ .
- (ii) The electron density on the terminal S atom is hardly altered by electron delocalisation compared to that of the free  $\text{MoS}_4^{2-}$ .
- (iii) Delocalised m.o.'s over the metal centres M' and M occur in the units  $\{\text{M}'\text{S}_2\text{MS}_2\text{M}'\}$ .

The electronic spectra of complexes with  $d^{10}$  central atom show essentially ligand internal transitions corresponding to those of the free thiometallate ions. Amongst the three ligand internal transitions the first ( $\nu_1$ ) and the third ( $\nu_3$ ) are more strongly disturbed compared to the second ( $\nu_2$ ) transition. The perturbation of the  $\nu_2$  band is more involved when  $\pi(\text{M}') - \text{L}$  interactions are predominant [21].

## 2. Vibrational Spectroscopy

The structure of the thiometallate complexes of the type  $[\text{M}'(\text{MS}_4)_2]^{2-}$  have been determined by IR spectroscopic investigations [6,10,12,83-85]. Complete normal coordinate analyses have been performed using the isotope substitution technique to produce

detailed information of the spectra of these complexes [86-90]. In all these cases, structures deduced by the technique have been confirmed by X-ray structural studies whenever suitable single crystals could be made. Outcome of these studies have now made it possible to characterise especially the bidentate nature of these ligands. The reduction of  $T_d$  symmetry of  $MS_4^{2-}$  free anion into  $C_{2v}$  microsymmetry when present as bidentate ligand results in the splitting of the symmetric and antisymmetric  $M-S$  stretching vibrations into two components [83]. In practice the terminal  $M=S$  groups are characterised by one or two vibrational frequencies between 480 and 510  $cm^{-1}$  and the bridging  $M-S$  groups by frequencies in the range 430 to 460  $cm^{-1}$ . In dinuclear species like  $[Cl_2FeMoS_4]^{2-}$ , the  $\nu(M-S_{br})$  and  $\nu(M-S_{term})$  vibrations are relatively characteristic. However,  $\nu_{as,term}$  is the most, and  $\nu_{s,br}$  the least characteristic vibration [86-88,90]. The preferential sulphur coordination over oxygen in ligands of the type  $MO_2S_2^{2-}$  could be easily seen by comparing the spectra of complexes using  $MO_2S_2^{2-}$  and  $MS_4^{2-}$  ligands. The terminal  $\nu(M-O)$  and  $\nu(M-S)$  could be easily identified along with  $\nu(M-S_{br})$  in these complexes. A representative example to demonstrate the ease in identifying these vibrations is presented in Figure 1.11. The characteristic vibrational spectral data for the series of complexes are presented in Table 1.1 for comparison. The Raman spectra of these complexes show characteristic symmetric vibration, especially  $\nu(M-S_{br})$  symmetric vibration. Symmetric  $M'-S$  vibration could also be identified (Table 1.1).

As the ligand internal transitions in thiomolybdate complexes correspond roughly to free  $\text{MoS}_4^{2-}$  one can obtain resonance Raman Spectra for this free anion as well as for its complexes. The totally symmetric  $\nu(\text{Mo-S})$  stretching vibrations of the  $\text{MoS}_4$  chromophore are significantly intensified. Using this technique significant distinction can be made between doubly bridging and bidentate ligands. One of the most important contribution of this technique is its use as a unique and sensitive probe for doubly bridging ligand [91]. Resonance Raman is a sensitive probe, also for the detection of transition metal centres in biological system [92,93].

### 3. X-ray Diffraction Studies

The inherent question about these polynuclear complexes lies in the understanding of any  $\text{M}'\text{-M}$  interaction, that is, is there any bonding interaction between these two metals? As described earlier, if the separation of two metals is ca.  $1.8 \text{ \AA}$ , appreciable overlap can occur between the metal d orbitals of appropriate symmetry. Unambiguous information regarding this bonding interaction can not be obtained in a straight forward manner by the use of crystallographic data only. The length of the  $\text{M}'\text{-M}$  separation is very much dependent on the  $\text{M}'\text{-S-M}$  angle which remains relatively invariant in most of the structures of complexes containing iron ( $\text{M}'$ ) with the variation of other substituent groups coordinated to iron. The Fe-S bond

length in complexes of this type containing thiomolybdate as ligand are slightly shorter than the Fe-S bond in the pure ferrous complex anion  $[\text{Fe}(\text{SPh})_4]^{2-}$ . If this bond shortening in multinuclear complexes is considered as an indication of Fe-M interaction, the consequence of this transfer of electron to the  $\text{MS}_4^{2-}$  units would affect the M-S bond length. However, the crystallographic data suggest insignificant lengthening of the M-S bond in the coordinated  $\text{MS}_4^{2-}$  compared to the M-S bonds in free  $\text{MS}_4^{2-}$  anions.

The short M'-M distances in the  $[\text{Ni}(\text{MoS}_4)_2]^{2-}$  and  $[\text{Zn}(\text{MS}_4)_2]^{2-}$  complexes may thus indicate extensive M'-M charge transfer leading thereby to M'-M bonding which are not very likely to occur in these complexes.

Thus, the short M'-S-M angle primarily dictates the M'-M distances. However, interesting observation can be made by comparing these structural parameters for the complex  $[\text{Co}(\text{WS}_4)_2]^{2-}$  and the corresponding reduced species,  $[\text{Co}(\text{WS}_4)_2]^{3-}$ . In the reduced species the longer W-S bond lengths compared to those of the starting complex clearly indicate a delocalisation of charge towards the tetrathiomallate units [94]. This electron delocalisation can also be supported by the reversible redox behaviour of these systems [14,95]. Furthermore, resonance Raman Spectroscopic results can also be incorporated with the strong electronic interaction between the heterometal centres. Representative X-ray structural parameters of some of the complexes are presented in Table 1.2.

TABLE 1.2

## X-RAY STRUCTURAL PARAMETERS OF SOME TETRATHIOMETALLATO COMPLEXES

Compound	M-S <sub>br</sub>	M-S <sub>term</sub>	M...M'	M'-S	M'-S-M	Reference
(NEt <sub>4</sub> ) <sub>2</sub> [(PhS) <sub>2</sub> Fe(MoS <sub>4</sub> )]	2.246 Å	2.154 Å	2.750 Å	2.250 Å	75.5°	96
(PPh <sub>4</sub> ) <sub>2</sub> (N(C <sub>7</sub> H <sub>7</sub> )Me <sub>3</sub> )[Cl <sub>2</sub> Fe(MoS <sub>4</sub> )]		a	2.775	2.299	75.6	23, 24
(PPh <sub>4</sub> ) <sub>2</sub> (N(C <sub>7</sub> H <sub>7</sub> )Me <sub>3</sub> )[Cl <sub>2</sub> Fe(WS <sub>4</sub> )]		a	2.808	2.306	75.3	24
(PPh <sub>4</sub> ) <sub>2</sub> [(Cl <sub>2</sub> Fe) <sub>2</sub> MoS <sub>4</sub> ]	2.204	a	2.775	2.295	76.1	26.9
(PPh <sub>4</sub> ) <sub>2</sub> [Co(WS <sub>4</sub> ) <sub>2</sub> ]	2.219	2.139	2.798	2.263	76.9	97, 98
(PPh <sub>4</sub> ) <sub>2</sub> [Ni(MoS <sub>4</sub> ) <sub>2</sub> ]	2.227	2.151	2.798	-	-	7, 98
(AsPh <sub>4</sub> ) <sub>2</sub> [Ni(WS <sub>4</sub> ) <sub>2</sub> ]	2.232	2.151	2.817	2.333	78.2	21, 98
(PPh <sub>4</sub> ) <sub>2</sub> [Zn(WS <sub>4</sub> ) <sub>2</sub> ]	2.233	2.156	2.929	-	-	98, 99

a, not determined because of statistical disorder.

#### 4. X-ray Photoelectron Spectroscopy

In recent years photoelectron spectroscopy has been used to know the binding energy of all the electrons in a species. This type of primary information which, in principle, the spectroscopy can provide, is of fundamental importance for formulating theories of the behaviour of atoms in bonding to form molecules or solids. The secondary information which this spectroscopy can provide is to know the trends in the photoelectron spectra in series of related families of substances correlation of geometries of molecules, the operation of substituent electronic effects, the importance and electronic role of ligands in coordination compounds, adsorbed surface phenomena and many other factors. These are very much helpful for a chemist [100].

The principle of photoelectron spectroscopy is known since 1905 through the Einstein Photoelectric law [101] which is essentially an energy balance, relating the energy of the impacting photon,  $h\nu$ , with the ionisation potential,  $I$ , of the target and the kinetic energy, K.E., of the ejected photoelectron:

$$\text{K.E.} = h\nu - I .$$

Depending on the nature of the photon source the photoelectron spectroscopy which is used in chemistry is divided into (i) UPS (UV-Photoelectron Spectroscopy) by which information about valence electron may be obtained, and (ii) XPS (X-ray-

Photoelectron Spectroscopy) which gives core electron information.

On analysis of the kinetic energy of the photoelectron one can get the modified equation

$$E_B = h\nu - K.E. (-E_W)$$

where  $E_B$  = Binding Energy, and

$E_W$  = Work Function.

Chemical information from the binding energy difference of inner electron which is influenced by the mode of bonding in various compounds can be correlated as can be done by NMR and Mössbauer spectroscopy.

In reality the change in binding energy for a particular atom bonded in a compound with respect to the binding energy of the free atom or free molecule is measured. Under these conditions a positive shift corresponds to positive effective charge of the atom in the compound and the negative shift corresponds to the negative effective charge. Qualitatively using this simple correlation procedure one can get information about the oxidation state of a particular atom in a compound in terms of classical chemical concepts. The problem can be viewed in the following way:

Cu(I) containing compounds when subjected to XPS studies show copper  $2p_{3/2}$  signal. The binding energy levels of this

copper core electron are substantially different when Cu(II) is present. In the native copper thionein protein a large and homogeneous copper  $2p_{3/2}$  signal appeared at 932.3 eV suggesting the exclusive presence of Cu(I). Oxidation of this protein with hydrogen peroxide caused the appearance of two signals at 940.0 eV and 942 eV which are attributable to the presence of Cu(II). Thus, the conversion of Cu(I) into Cu(II) could be unequivocally shown. These results are parallel to the corresponding data obtained for the sulphur 2p levels. The appearance of sulphur core electron signal at 162.7 eV is very much identical to the presence of thiolate type of sulphur coordinated to Cu(I).  $H_2O_2$  treated sample shows a dramatic shift of the sulphur 2p signal to 167.9 eV which is suggestive of all sulphur being oxidised to  $RSO_3^-$ . The intermedial sulphur redox states could also be recorded at 163.7 and 166.6 eV which were attributed to  $RSSR$  and  $RSO_2^-$  [102].

The above findings amply demonstrate the use of this methodology even in biological problems. The 2p binding energy for elemental sulphur is found to be 164.2 eV [103]. When sulphur containing functional groups have sulphur in reduced state like  $S^{2-}$ ,  $-C-S^-$ ,  $-C-S-C-$  or  $C=S$ , the 2p binding energy falls in the range 162.0 - 163.5 eV [104]. The corresponding value for this in  $Na_2S$  is 162.0 and in  $Na_2S_2$  162.4 eV. In the thio-metallate anion this value for sulphide sulphur falls in the range 162.2 - 163.5 eV [105].



Thus one can distinguish the status of sulphur bound in a compound with respect to its formal oxidation state [106]. If a change in effective charge of sulphur when present in such form can be correlated with a change of the effective charge on the central atom, one can deduce a charge transfer mechanism between these two atoms.

For molybdenum, signals obtained from the 3d shell electrons show a normal splitting for  $J = 5/2$  and  $J = 3/2$ . Normally when sulphur is present in a molybdenum compound, the sulphur  $2s_{1/2}$  signal appears nearby the molybdenum signals and can be observed as a shoulder at calculated ca. 228.2 eV. For molybdenum, the  $3d_{5/2}$  and  $3d_{3/2}$  signals also can be correlated with a formal oxidation state of Mo. The correlation of this nature is shown in Figure 1.12 with a series of molybdenum compounds in different formal oxidation states. The correlation of the binding energy and oxidation state is also shown for a series of molybdenum compounds in Table 1.3.

## 5. Other Physical Studies

When the central metal of these polynuclear complexes is of the open shell type, the magnetic moment values expectedly suggest the nature of coordination of the central atom. The magnetic moment values do suggest the electron delocalisation in complexes containing tetrahedral  $CoS_4$  chromophore and this behaviour is more clearly expressed in  $[Fe(MoS_4)_2]^{3-}$  [13, 19, 20].

TABLE 1.3

OXIDATION STATES AND BINDING ENERGIES OF SOME MOLYBDENUM COMPOUNDS

Compound	Oxidation State	Mo $3d_{5/2}$ $E_B$ [eV]	Reference
$(NH_4)_2 MoS_4$	+6	231.7	105
$[MoOS_2(dtc)_2]$	+6	231.3	107
$[MoS_2Cl_3]$	+5	231.3	107
$(NH_4)_2 [MoO_2(S_2)_6]$	+5	230.3	107
$(NMe_4)_2 [MoO_2S_2(S_2)_2]$	+5	230.6	107
$(NH_4)_2 [Mo_3S(S_2)_6]$	+4	230.8	107
$[Mo_3S_7Cl_4]$	+4	230.1	107
$(NH_4)K[Mo_4(NO)_4S_{12}O]$	+2	229.7	107
$(NH_4)_4[Mo_4(NO)_4S_{13}]$	+2	230.1	107
Mo	0	226.1	108
$[Mo(CO)_6]$	0	226.6	108

It is interesting to note that the ESR spectrum of this trianion is similar to that of the MoFe-cofactor of nitrogenase [19,20]. In  $[(Cl_2Fe)_2MS_4]^{2-}$  complexes the magnetic moments are lower than expected for two non-interacting high spin Fe(II) ions which can be interpreted due to antiferromagnetic exchange which is appreciably weaker in W-trimetallic complex than in the Mo analogue [109].

The  $^{57}Fe$  isomer shifts of the  $MS_4^{2-}$  complexes using Mossbauer spectroscopy suggest intermediate values reported for the tetrahedral Fe(II) $S_4$  and Fe(III) $S_4$  chromophores [57b]. Thus, the formal oxidation state of Fe between II and III in these complexes represent direct evidence for Fe — M charge transfer. These types of measurements have been widely used for the double cubane and related Fe-Mo-S complexes. Besides, the NMR technique has also been used to study the ligational exchange reaction of the  $Fe_3MoS_4$  core [63]. For a closed shell central metal especially Cu(I), use can be made of NMR technique when phosphine derivatives are used as coligand. Some studies have been made in this regard to elucidate structural information of a few complexes especially when the X-ray crystal structure analyses could not be made due to unavailability of suitable crystals [110].

## CHAPTER II

### SCOPE OF THE WORK

The exploitation of thiometallate anions, especially  $\text{MoS}_4^{2-}$  and  $\text{WS}_4^{2-}$  as ligand, started just a decade ago [6]. The ligand properties of these anions to produce multimetal complexes are explored at the start from structural point of view and for their unusual electronic properties. Thus a series of bis-tetrathiometallate complexes have been characterised where the central metal, in most of the cases, exists formally in +2 oxidation state [83]. They are essentially synthesised in aqueous medium and the resultant complexes are precipitated by bulky quaternary phosphonium or arsonium cations. Spectroscopic investigations of the aqueous solutions thus obtained before the

precipitation of a species by suitable cation do suggest several other species, the exact chemistry of which are not known. Thus, for example, when  $\text{Fe}^{2+}$  is treated with  $\text{WS}_4^{2-}$  in aqueous medium, an orange coloured solution is obtained which on addition of  $[\text{PPh}_4]\text{Cl}$ , leads to the separation of a green precipitate of  $[\text{PPh}_4]_2[\text{Fe}(\text{WS}_4)_2]$  [11].

Another class of interesting reactions of tetrathio-metallate is their condensation reaction and the formation of polythioanions wherein the condensation reaction proceeds with redox process. Thus, both the heterothioanions and polythio-metallates are recognised.

The first prediction about the possible role of thio-metallate in nitrogenase has been made in 1977 wherein the reactivity between  $\text{Fe}^{2+}$  and  $\text{MS}_4^{2-}$  ions is studied in aqueous medium [11]. This part of research gained momentum by the unique observation made by Zumft that  $\text{MoS}_4^{2-}$  could be isolated as hydrolysis product of the nitrogenase [18]. These observations prompted many authors to extend this type of reactivity to synthesise newer species even in non-aqueous media (vide supra). However, one of the most important reactions in aqueous medium is still not clearly understood and this is the reaction between aquated  $\text{Fe}^{2+}$  and the solution of  $\text{MoS}_4^{2-}$  anion. The first study on this system shows the formation of the polymeric species of approximate composition  $[\text{PPh}_4]_2[\text{Fe}(\text{MoS}_4)_2]$  [11].

Interaction between S containing iron compound with tetrathio-molybdate in non-aqueous media leads to the formation of discrete anion  $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ . It has been presumed in such reactions that the S containing organic ligand reduces the central iron which is formally in +1 oxidation state [19, 20].

However, the generation of the same species can be achieved using the iron source as ferrous oxalate, which may suggest that the oxalate group can function as the reducing species. Interestingly, when the reaction in the system  $\text{Fe}^{2+}/\text{MoS}_4^{2-}/\text{H}_2\text{O}$  is carried out without the immediate addition of tetraphenylphosphonium salt,  $[\text{Fe}(\text{MoS}_4)_2]^{3-}$  is formed which could be isolated in good yield when the solvent medium used is  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  in 1:1 ratio (vide supra). Thus, besides its ligation-al property,  $\text{MoS}_4^{2-}$  can serve as a reducing species in the system. In pure water (as solvent) polymeric species are formed and this is by large a general phenomenon, also encountered with other metals like Ni and Co and the extent of polymerisation is not large with the latter metal ions [21].

The reactivities of thiometallates to produce heterothio-anions largely differ for the 'nitrogenase element iron' in aqueous medium. And this difference between the reactivities of  $\text{MoS}_4^{2-}$  and  $\text{WS}_4^{2-}$  do suggest the biorelevance of  $\text{MoS}_4^{2-}$  over the other.

Interactions of tetrathiometallate with copper is another set of important reactions having biorelevance. Cupric ion

forms several complexes with sulphur containing ligands retaining its +2 oxidation state. Contrary to this, thiometallates react with cupric with its immediate reduction to cuprous state whereas free sulphide ion leads to the immediate precipitation of CuS. This reducing capability of  $S^{2-}$  bound to metal ion in the series  $[Mo_{4-n}S_n]^{2-}$  ( $M = Mo, W$ ) is retained.

In many copper proteins, especially having thionein bound copper the formal oxidation state of copper is believed to be +1. Thus, the interaction between cupric and thiometallate to produce cuprous is of biorelevance as it is believed that the metabolic activity of copper is facilitated when present in cuprous state rather than in the cupric one [111].

The reaction containing  $Cu^{2+}/MoS_4^{2-}/H_2O$  system produces the insoluble polymeric species of the unit,  $[CuMoS_4]^-$  and X-ray structural characterisation of the corresponding  $NH_4^+$  salt shows the presence of chains of  $CuS_4$  and  $MoS_4$  tetrahedra connected via the edges [8]. The corresponding tungsten analogue  $[CuWS_4]^-$  is also known [112]. In these systems the  $MS_4^{2-}$  ion acts formally as a doubly bridging ligand.

In the quest of preventing this polymerisation and backed by the knowledge of the reactivity of these thiometallates with other metal ions including iron as stated earlier, some non-aqueous reactions were undertaken. The first phase of this type of reaction started with the use of bulky substituted phosphine ligands which are strongly bound to copper(I) and thus could

cause the termination of polymerisation. Using this methodology Müller and coworkers characterised complexes of the following type [21]:

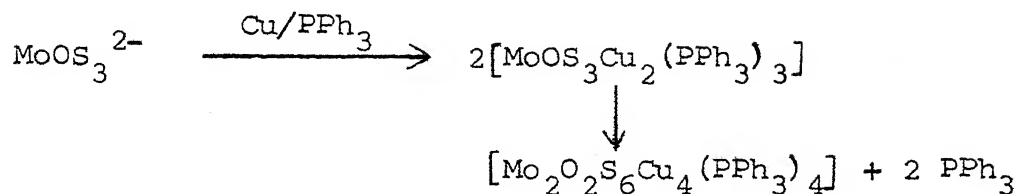
- (i)  $\left\{ \text{Cu}_3\text{MS}_3\text{Cl} \right\} (\text{PPh}_3)_4 \text{X}$  ( $\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{O}$ ).
- (ii)  $\left\{ \text{M}'_4\text{M}_2\text{S}_6 \right\} (\text{PR}_3)_4 \text{X}_2$  ( $\text{M}' = \text{Cu}, \text{Ag}; \text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{O};$   
 $\text{R}_3 = \text{Ph}_3, (\text{C}_7\text{H}_7), \text{MePh}_2$ ).
- (iii)  $\left[ (\text{PR}_3)_n \text{M}'_2 (\text{MS}_4) \right]$  ( $\text{M}' = \text{Cu}, \text{Ag}, \text{Au}; \text{M} = \text{Mo}, \text{W};$   
 $\text{R}_3 = \text{Ph}_3, \text{MePh}_2; n = 2, 3, 4$ ).

The synthetic procedures to obtain these complexes is very much dependent on the condition imposed, and in most of the cases more than one compound is formed. As a source of copper, cupric is invariably used which under the reducing environment containing substituted phosphines and thiometallate, is thus changed to cuprous state in the complexes. For the synthesis of silver analogue the source of silver used is the readily available Ag(I) salt. Structurally, these multinuclear complexes show interesting geometries which are not even available with the pure Cu(I) compounds. Thus, the cubane structural variety (as in (i)) can be thought to be derived from  $(\text{CuIPPh}_3)_4$  [69].

Similarly, type (iii) resembles structurally the complexes  $\text{Cu}_2\text{X}_2\text{L}_4$  and  $\text{Cu}_2\text{X}_2\text{L}_3$  where  $\text{X} = \text{halogen}$  &  $\text{L} = \text{tertiary phosphine}$  [68]. Structural type (ii) has no analogue in pure copper compounds and this cage structure, which is formed by fusing two



six membered  $\{S_2Ag_2S_2Mo\}$  rings has been established by isolating a compound consisting of the half structure of the cage which when allowed to react in solution for a longer time tends to produce the more stable cage compound by a psuedo dimerisation process as shown below [113]:



The use of P-donors to prevent polymerisation prompted studies on the interaction between polymeric CuCN and  $MoS_4^{2-}$ . Once again several species exist in this system which can be trapped selectively by the suitable use of the cation depending on its size (vide supra).

Müller and coworkers have proposed the above structurally characterised complexes as possible model compounds in Cu-Mo antagonism. Recent studies on this interaction by Mills [114] and Suttle [115] provided indirect evidence for the role of  $MoS_4^{2-}$  for this sulphur dependent interaction.

Two important objections may be raised to accept the characterised complexes of Cu-Mo-S as possible models for Cu-Mo antagonism:

(i) Presence of P-donors like tertiary phosphine derivatives under physiological conditions,

(ii) Necessity of non-aqueous medium which is a guiding force to isolate these multinuclear complexes.

From the above stated objections it is apparent that the polymeric species  $\text{NH}_4[\text{CuMoS}_4]$  is the closest possible approach as a model in this system. Amongst the monomeric and the polymeric complexes,  $(\text{PPh}_4)_2[\text{NCCu}(\text{MoS}_4)]$  and  $(\text{NMe}_4)_2[\text{NCCu}(\text{MoS}_4)] - \{\text{CuCN}\}$ , the polymeric variety suggests cyano-bridged bonding where the copper site is alternately bound through N-atom. From the point of view of protein interaction with these systems, this finding has some relevance regarding the N-donor site to copper. However, the Cu-C bond which is alternately present in this structure and also in the monomeric variety has no relevance so far the protein interaction is concerned.

Restricting the argument with protein interaction in this system, modelling of the compound could be made using ligands having donor atoms like N, O or S. Furthermore, simulation in the rumen environment has shown that when  $\text{MoS}_4^{2-}$  is there, hydrolysis takes place to give an equilibrium mixture of  $\text{MoS}_4^{2-}$  (67%),  $\text{MoOS}_3^{2-}$  (26%) and  $\text{MoO}_2\text{S}_2^{2-}$  (6%) together with the formation of  $\text{HS}^-$  and  $\text{H}_2\text{S}$  [116]. Suttle suggested that the trace amounts of  $\text{HS}^-$  and  $\text{H}_2\text{S}$  thus formed will not significantly affect the interactions occurring in the rumen [115]. Although this experiment has been done in vitro, which suggests the above hydrolysis into a cut off simulated rumen environment. In vivo a continuous supply of sulphide ion concentration may reverse

this hydrolysis. Chemically, the formation of tetrathiomolybdate by the interaction of  $\text{MoO}_4^{2-}$  and  $\text{H}_2\text{S}$  in ammoniacal medium supports the dependence of the intermediate mixed oxo-thio-metallate species on the reaction time and  $\text{H}_2\text{S}$  concentration [117].

Bearing the above facts in mind suitable ligands having donor atom like proteins may be allowed to interact with Cu(I) and tetrathiomolybdate. Copper forms cubane type of compounds like  $(\text{CuXpy})_4$  which is identical structurally to the corresponding tertiary phosphine analogue [70]. The corresponding Cu-Mo-S compound with tertiary phosphine is known; however, the alternative chair form of the tetranuclear species is structurally retained when CuCl alone is bound to  $\text{MoS}_4^{2-}$  (vide supra). Hence it would be interesting to explore the possibility of obtaining similar type of compound using pyridine nitrogen as the donor. Unsymmetrical trinuclear complexes with the metal frame as shown in Figure 1.7b are known for Cu system, whereas the silver gives the symmetrical frame too (Figure 1.7a).

In all these complexes L is invariably tertiary phosphine. The similar Cu-Mo-S species with the use of N-donors would be a closer approach towards the involvement of protein interaction in the system.

The work-up manipulations to follow these reaction courses would be straightforward interaction of cuprous salt as a source of copper, appropriate ligand and  $\text{MoS}_4^{2-}$  in non-aqueous

media, so that, polymerisation, hydrolysis and the involvement of  $\text{MoS}_4^{2-}$  to reduce copper could be avoided.

This synthetic approach may be extended to other oxothiomolybdates to know the behaviour of the attachment of  $\text{Cu(I)}$  towards oxygen and sulphur. This is especially important when cubane type of structural variety is required in the series of tetrameric  $(\text{CuXL})_4$  species, where the mixed metal complex would require three sulphurs attached to molybdenum to serve as three vertices of the cubane core keeping another sulphur or oxygen attached to molybdenum free. The choice of several nitrogen donors ranging from monodentate to bidentate may be used to produce different structural variety depending on the actual nature of the ligand. Ambidentate ligands like thiocyanate may be used in which the donor site would parallel the donor sites in proteins. Thus, the knowledge of P-donor in the system can be extended not only to nitrogen donors but it could be extended to even arsenic donors to follow the trend in the series, N, P and As.

However, as discussed earlier if it is possible to transfer this methodology in aqueous medium, that would be definitely the closest approach to the biorelevance of such reactions. The only available stable species in aqueous medium for this system is the polymeric  $\text{NH}_4\text{CuMoS}_4$ . This is caused by the immediate reduction of cupric ion present in aqueous solution with  $\text{MoS}_4^{2-}$ . It would be interesting to see this reactivity between  $\text{Cu}^{2+}$

and  $\text{MoS}_4^{2-}$  when the availability of the free copper ion is sufficiently low. This could be achieved by the use of freshly precipitated  $\text{CuS}$  which, having very low solubility product, can serve the above purpose. Besides, freshly prepared species would show enhanced surface activity. Precipitated  $\text{CuS}$  is a potential candidate for the depletion of free copper for metabolism. However, in the rumen, if this is the only interaction for such depletion, the role of  $\text{MoS}_4^{2-}$  remains passive. From the chemical stand point one is tempted to think that if  $\text{H}_2\text{S}$  or  $\text{S}^{2-}$  is allowed to react with a mixture of cupric ion and  $\text{MoO}_4^{2-}$ , it is the insolubility of  $\text{CuS}$  which is going to control the reaction, and the first phase of the reaction would be the use of  $\text{H}_2\text{S}$  or  $\text{S}^{2-}$  to interact with free cupric ion. The interaction between  $\text{MoO}_4^{2-}$  and  $\text{S}^{2-}$  would start when the whole copper is precipitated as  $\text{CuS}$ . We do not know whether there is a mechanism involved in the rumen by which even insoluble  $\text{CuS}$  may not be wholly biologically unavailable. It has been observed that cupric oxide when served in the body can supply copper for metabolism. One might be tempted to think that even  $\text{CuS}$  is poorly available for metabolic activity, yet, it can go to participate in a more complex form with tetrathiomolybdate which is formed at the later stage thereby completely removing copper from the metabolic cycle.

Thus a study of such type of interaction between  $\text{Cu}^{2+}/\text{MoO}_4^{2-}/\text{H}_2\text{O}/\text{H}_2\text{S}$  at proper pH with or without donor ligand would be worth exploring.

The function of  $WS_4^{2-}$  or other oxothiotungstates as ligands parallels those of the corresponding molybdenum compounds. From synthetic point of view, the newer complexes which could be tried with the molybdenum system can also be tried with the corresponding tungsten ones. In the natural process, the incorporation of molybdenum suggests some special properties of molybdate system compared to tungstates. Thus, any difference between the reactivity of these two systems would reflect the cause for the natural selection of molybdenum over tungsten in biological system.

### CHAPTER III

#### EXPERIMENTAL

##### 3.1 Methods of Analysis and Work-up Manipulations

Carbon, hydrogen, nitrogen, sulphur and chlorine were analysed by microanalytical methods at I.I.T., Kanpur and University of Bielefeld, West Germany.\*

Copper and molybdenum were analysed by atomic absorption spectroscopic methods at University of Bielefeld, West Germany.\*

All the chemicals and solvents used, were of analytical grade. The solvents were dried before use by appropriate drying agents. Most of the syntheses were performed under inert atmosphere to avoid decomposition due to the air susceptible nature of thiometallates.

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\*Courtesy Prof. S. Sarkar.

Only freshly prepared cuprous salts and thiometallates were used for the syntheses. These were prepared according to literature methods as follows:

### 3.1a(i) Preparation of cuprous chloride

A solution of 7.6 g of anhydrous sodium sulphite,  $\text{Na}_2\text{SO}_3$ , in 50 ml water was added slowly at room temperature to a stirred solution of 10 g of Cu(II) chloride,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , in 10 ml of water. The mixture was stirred thoroughly when the copper(I) chloride settled readily and the supernatant liquid was faintly green. The contents were poured into about one litre of water containing about 1 g of sodium sulphite and 2 ml of conc. HCl. The mixture was stirred well and allowed to settle. After decantation of supernatant liquid the precipitate was quickly transferred to a sintered crucible attached to suction. The precipitate was washed with glacial-acetic acid, absolute alcohol and anhydrous ether with the precaution that a layer of washing liquid covered the salt all the time. The precipitate was transferred to a watch glass and placed in an oven ( $75-100^\circ$ ) for 25 minutes. The sample was preserved in an air tight bottle [118]. Yield  $\sim 85\%$ .

Anal. found: Cu, 64.5; Cl, 36.2%.

Calcd for  $\text{CuCl}$ : Cu, 64.2; Cl, 35.8%.



### 3.1a(ii) Preparation of CuSCN

4.0 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 100 ml of water. A few drops of dilute hydrochloric acid and slight excess (about 80 ml) of freshly prepared saturated sulphurous acid solution was added to it. The solution was diluted to 200 ml and heated nearly to boiling when freshly prepared ammonium thiocyanate solution was added slowly with constant stirring. When precipitation was complete, the contents were allowed to stand for two hours. The precipitate was filtered through sintered glass crucible and washed several times with water containing little amounts of ammonium thiocyanate and sulphurous acid. Final washings were done with 20% alcohol and dried at  $110-120^\circ$ . Yield  $\sim 85\%$ .

Anal. Found: C, 10.02; N, 11.49; Cu, 52.35; S, 26.40%.

Calcd for CuSCN: C, 9.88; N, 11.52; Cu, 52.26; S, 26.34%.

### 3.1b. Preparation of ammonium tetrathiomolybdate

A solution of 5 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 15 ml of water was prepared and treated with 50 ml of ammonia (d 0.94). Then  $\text{H}_2\text{S}$  was introduced. The solution first turned yellow, later deep red, and after half an hour a copious quantity of crystals, some of them well formed, precipitated suddenly. The crystals were washed with cold water, then with alcohol and ether, and dried in vacuum [118]. Yield  $\sim 70\%$ .

The compound gave characteristic band at  $470\text{ cm}^{-1}$  in the i.r. spectrum due to  $\nu(\text{Mo-S})$  [119].

### 3.1c. Preparation of $(\text{NH}_4)_2\text{WS}_4$

$\text{H}_2\text{S}$  was bubbled into an aqueous solution of 5 g sodium tungstate with excess of  $\text{NH}_3$ . The solution was kept under  $\text{H}_2\text{S}$  atmosphere for about four days when orange yellow crystals of  $(\text{NH}_4)_2\text{WS}_4$  separated out. The crystals were collected by suction filtration, washed with water, alcohol and ether respectively and vacuum dried [120]. Yield  $\sim 75\%$ .

The i.r. spectrum of the compound gave characteristic band at  $455\text{ cm}^{-1}$  due to  $\nu(\text{W-S})$  [119].

### 3.1d. Preparation of $\text{Cs}_2\text{MoOS}_3$

$\text{H}_2\text{S}$  was passed into a mixture of 15 ml of water and 15 ml of  $\text{NH}_3$  solution (d 0.94) containing 5 g ammonium molybdate. After addition of an excess of  $\text{CsCl}$  solution and acetic acid (upto pH 10) orange crystals of  $\text{Cs}_2\text{MoOS}_3$  separated out. The compound was suction filtered, washed with cold water, acetone and ether, respectively. It was vacuum dried and analysed [121]. Yield  $\sim 50\%$ .

The compound gave characteristic i.r. bands at  $862(\text{s})$ ,  $470(\text{s})$  and  $461(\text{m})\text{ cm}^{-1}$  due to  $\nu(\text{Mo-O})$  and  $\nu(\text{Mo-S})$  vibrations [119].

### 3.1e. Preparation of $\text{Cs}_2\text{WOS}_3$

Cesium chloride (3.4 g) was added to the aqueous solution of  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$  (3.2 g) and  $\text{H}_2\text{S}$  was introduced into the solution while keeping it cold in ice. After few minutes yellow crystals of  $\text{Cs}_2\text{WOS}_3$  separated out. The crystals were collected by filtration through suction, washed with water, alcohol and ether, respectively and dried [122]. Yield  $\sim 60\%$ .

The i.r. spectrum of the compound gave characteristic bands at 878(s), 474(w) and 451(s)  $\text{cm}^{-1}$  due to  $\nu(\text{W-O})$  and  $\nu(\text{W-S})$  vibrations [119].

### 3.1f. Preparation of $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ and $(\text{NH}_4)_2\text{WO}_2\text{S}_2$

These compounds were prepared by the method described by Müller and coworkers.

5 g of sodium molybdate (or tungstate) was dissolved in 25% ammonia solution and was cooled in ice.  $\text{H}_2\text{S}$  was introduced into this ice-cold solution when after few minutes insoluble orange yellow  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  (or yellow  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$ ) separated out. The crystalline solid was filtered through suction, washed with water, alcohol and ether and dried [122]. Yield  $\sim 60\%$ .

The compounds gave characteristic i.r. bands at 861(s), 840(s), 470(s) and 450(s)  $\text{cm}^{-1}$  responsible for  $\nu(\text{Mo-O})$  and  $\nu(\text{Mo-S})$  vibrations and at 886(s), 848(s), 454(s) and 442(s)  $\text{cm}^{-1}$  due to  $\nu(\text{W-O})$  and  $\nu(\text{W-S})$  vibrations [122].

### 3.2 Synthesis of Binuclear Species

#### 3.2a. Preparation of $\text{PPh}_4[(\text{o-phen})\text{CuMoS}_4]$

One equivalent each of ammonium tetrathiomolybdate (0.26 g), o-phenanthroline (0.198 g) and CuSCN (0.12 g) were taken in 15 ml of DMF under stirring condition whereby a clear red solution was obtained after an hour. One equivalent of tetraphenylphosphonium chloride dissolved in minimum amount of DMF, was added into it. The clear red solution was filtered to remove traces of insoluble matter. Into this, dropwise diethyl ether (8 ml) was added to initiate a cloudiness and this was kept in a stoppered flask. On overnight standing, red microcrystalline compound separated out which was filtered under suction, washed quickly with little DMF and finally with ether and vacuum dried. Yield ~ 56%.

Anal. found: C, 53.88; H, 3.26; N, 3.50; Cu, 7.42;  
Mo, 12.50; S, 16.20%.

Calcd for  $\text{CuC}_{36}\text{H}_{28}\text{N}_2\text{PMoS}_4$ : C, 53.56; H, 3.47; N, 3.47;  
Cu, 7.87; Mo, 11.90; S, 15.87%.

#### 3.2b. Preparation of $\text{PPh}_4[(\text{o-phen})\text{CuWS}_4]$

The complex was synthesised by using 0.35 g  $(\text{NH}_4)_2\text{WS}_4$ , 0.198 g o-phenanthroline and 0.12 g CuSCN applying the same procedure as adopted for its molybdenum analogue. The compound was washed with DMSO followed by dichloromethane and diethyl-ether. It was vacuum dried and analysed. Yield ~ 60%.

Anal. Found: C, 47.96; H, 3.51; N, 3.46; Cu, 7.85;  
S, 14.15%.

Calcd for  $\text{CuC}_{36}\text{N}_2\text{PWS}_4$ : C, 48.30; H, 3.13; N, 3.13;  
Cu, 7.10; S, 14.31%.

### 3.2c. Preparation of $(\text{PPh}_4)_2[\text{NCSCuMoS}_4]$

Method A: One equivalent of tetraphenylphosphonium tetrathiomolybdate (0.45 g) was dissolved in DMF (15 ml). Into this, solid, freshly prepared CuSCN (one equivalent 0.060 g), was added in portions with stirring. After two hours most of the solid CuSCN was dissolved. The mixture was then filtered to remove undissolved solid matter and a little diethylether was added dropwise to start precipitation which on overnight standing precipitated the product. This was filtered under suction, washed quickly with a little portion of DMF and finally with diethylether and vacuum dried. Yield ~45%.

Anal. Found: C, 58.02; H, 3.50; N, 2.00; Cu, 6.52;  
Mo, 10.20; S, 15.25%.

Calcd for  $\text{CuC}_{49}\text{H}_{40}\text{NP}_2\text{MoS}_5$ : C, 57.45; H, 3.91; N, 1.37;  
Cu, 6.20; Mo, 9.38; S, 15.63%.

Method B: One equivalent of  $(\text{PPh}_4)_2\text{MoS}_4$  (0.45 g) was taken in a stoppered flask and 50 ml acetonitrile was added into it. This was magnetically stirred for 15 minutes to get a clear red

solution. Into this, one equivalent of freshly prepared  $\text{CuSCN}$  (0.060 g) was added portionwise with stirring to get the solid dissolved before each addition. After three hours of stirring almost a clear solution was obtained which was filtered. Into the filtrate about 10 ml of diethylether was added with stirring to keep the solution still clear. (Addition of excess of diethylether to start local precipitation without stirring was avoided as that would lead to appearance of powdery form of the desired compound). The clear solution was kept in a stoppered flask for 2-3 days whereby crystalline red compound was separated out. This was filtered, washed with acetonitrile and finally with diethylether and vacuum dried. Yield ~65%.

Anal. Found: C, 58.32; H, 3.62; N, 2.06; Cu, 6.82;  
Mo, 10.30; S, 15.52%.

Calcd for  $\text{CuC}_{49}\text{H}_{40}\text{N}_2\text{MoS}_5$ : C, 57.45; H, 3.91; N, 1.37;  
Cu, 6.20; Mo, 9.38; S, 15.63%.

### 3.2d. Preparation $(\text{PPh}_4)_2[\text{NCSCuWS}_4]$

The procedure adopted in method B for the synthesis of its molybdenum analogue was followed for the synthesis of this compound. 0.50 g of  $(\text{PPh}_4)_2\text{WS}_4$  was used in place of its molybdenum counterpart. The compound was washed with acetonitrile followed by diethylether, vacuum dried and analysed. Yield ~60%.

Anal. Found: C, 52.52; H, 3.91; N, 2.52; Cu, 5.25;  
S, 16.02%.

Calcd for  $\text{CuC}_{49}\text{H}_{40}\text{NP}_2\text{WS}_5$ : C, 52.90; H, 3.60; N, 1.26;  
Cu, 5.71; S, 14.39%.

### 3.3 Synthesis of Trinuclear Species

#### 3.3a. Preparation of $[(\text{o-phen})_2\text{Cu}_2\text{MoS}_4]$

One equivalent freshly prepared cuprous chloride (0.099 g) and one equivalent o-phenanthroline (0.198 g) were taken together in DMSO (10 ml). Into this, a solution of half equivalent of ammonium tetrathiomolybdate (0.13 g) dissolved in 10 ml of DMSO was added. The mixture was occasionally stirred once or twice to dissolve the suspended cuprous chloride to get almost a clear solution which was quickly filtered. The filtrate was kept undisturbed whereby red microcrystalline compound was separated out within two hours. This was suction filtered, washed with DMSO, dichloromethane and finally with diethylether. The compound was vacuum dried and analysed. Yield ~50%.

Anal. Found: C, 39.95; H, 2.35; N, 8.02; Cu, 17.80;  
Mo, 13.76; S, 18.34%.

Calcd for  $\text{Cu}_2\text{C}_{24}\text{H}_{16}\text{N}_4\text{MoS}_4$ : C, 40.51; H, 2.25; N, 7.88;  
Cu, 17.86; Mo, 13.50; S, 18.00%.

#### 3.3b. Preparation of $[(\text{o-phen})_2\text{Cu}_2\text{WS}_4]$

This compound was synthesised analogously as described above just by using ammonium tetrathiotungstate (0.18 g)

instead of ammonium tetrathiomolybdate. The compound was obtained as orange microcrystalline solid. Yield ~ 55%.

Anal. Found: C, 36.82; H, 2.32; N, 7.62; Cu, 16.35;  
S, 16.51%.

Calcd for  $\text{Cu}_2\text{C}_{24}\text{H}_{16}\text{N}_4\text{WS}_4$ : C, 36.05; H, 2.00; N, 7.01;  
Cu, 15.89; S, 16.02%.

### 3.3c. Preparation of $[\text{Cu}_2\text{As}_3(\text{C}_6\text{H}_5)_9\text{MoS}_4]$

An acetonitrile (50 ml) solution of two equivalents freshly prepared CuCl (0.20 g) and three equivalents of triphenylarsine (0.92 g) was added into a solution of  $(\text{NH}_4)_2\text{MoS}_4$  (one equivalent 0.26 g) in DMF (10 ml) to get a clear red solution on stirring. After half an hour the solution was filtered and the filtrate was just covered by a layer of diethylether which was added slowly and cautiously. On standing overnight, diffusion of the two layers resulted in appearance of the product in crystalline form. This was filtered under suction, washed with acetonitrile followed by diethylether and vacuum dried. Yield ~ 50%.

Anal. Found: C, 50.98; H, 3.60; Cu, 10.56; Mo, 7.82;  
S, 10.25%.

Calcd for  $\text{Cu}_2\text{C}_{54}\text{H}_{45}\text{As}_3\text{MoS}_4$ : C, 51.06; H, 3.55; Cu, 10.01;  
Mo, 7.57; S, 10.09%.



### 3.3d. Preparation of $[\text{Cu}_2\text{As}_3(\text{C}_6\text{H}_5)_9\text{WS}_4]$

The complex was synthesised in an analogous manner as described above for its molybdenum analogue. The only difference was the use of 0.35 g of  $(\text{NH}_4)_2\text{WS}_4$  in place of  $(\text{NH}_4)_2\text{MoS}_4$ . The compound thus obtained was washed with acetonitrile and diethylether, dried in vacuum and analysed. Yield ~ 62%.

Anal. Found: C, 48.02; H, 3.26; Cu, 9.58; S, 9.02%.

Calcd for  $\text{Cu}_2\text{C}_{54}\text{H}_{45}\text{As}_3\text{WS}_4$ : C, 47.75; H, 3.32; Cu, 9.36; S, 9.43%.

### 3.3e. Preparation of $[(\text{o-phen})_2\text{Cu}_2\text{MoO}_2\text{S}_2]$

One equivalent each of CuCl (0.10 g), o-phenanthroline (0.20 g) were taken in DMSO (20 ml). Into this, half equivalent  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  (0.12 g) was added and the resulting mixture was stirred for an hour whereby most of the solid reactants dissolved. The solution was filtered and into the filtrate, a mixture of dichloromethane and diethylether (1:1) was added to start the precipitation of the complex. The precipitation was completed on overnight standing. The product was filtered under suction, washed with DMSO followed by dichloromethane and finally with diethylether. The vacuum dried compound was analysed. Yield ~ 50%.

Anal. Found: C, 42.56; H, 2.54; N, 8.02; Cu, 18.23;

Mo, 14.56; S, 10.05%.

Calcd for  $\text{Cu}_2\text{C}_{24}\text{H}_{16}\text{N}_4\text{MoO}_2\text{S}_2$ : C, 42.42; H, 2.36; N, 8.25;  
Cu, 18.70; Mo, 14.14; S, 9.43%.

### 3.3f. Preparation of $[(\text{o-phen})_2\text{Cu}_2\text{WO}_2\text{S}_2]$

The compound was prepared by the method described above for its molybdenum analogue by using 0.16 g of  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$  in place of  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ . The compound obtained was filtered by suction, washed with DMSO, dichloromethane and diethylether, vacuum dried and analysed. Yield  $\sim 62\%$ .

Anal. Found: C, 38.04; H, 1.98; N, 7.50;  
Cu, 17.02; S, 8.45%.

Calcd for  $\text{Cu}_2\text{C}_{24}\text{H}_{16}\text{N}_4\text{WO}_2\text{S}_2$ : C, 37.55; H, 2.09; N, 7.30;  
Cu, 16.56; S, 8.34%.

## 3.4 Synthesis of Tetranuclear Species

### 3.4a. Preparation of $[\text{Cu}_3\text{As}_3(\text{C}_6\text{H}_5)_9\text{ClMoS}_4]$

The analogous method described in the synthesis of  $[\text{Cu}_3\text{As}_3(\text{C}_6\text{H}_5)_9\text{ClMoOS}_3]$  (vide infra) could not be applied here due to the strong formation tendency of  $[\text{Cu}_2\text{As}_3(\text{C}_6\text{H}_5)_9\text{MoS}_4]$ . Hence a modified method as described by Müller and coworkers for the synthesis of the corresponding triphenylphosphine analogue was followed. Three equivalents each of freshly prepared CuCl (0.3 g) and  $\text{AsPh}_3$  (0.92 g) were taken in 20 ml of dichloromethane and stirred for an hour to get a clear solution. One equivalent of ammonium tetrathiomolybdate (0.26 g) was dissolved in 10 ml of

water and both the solutions were taken together in a separatory funnel. The mixture was shaken vigorously for a minute and allowed to stand. The dichloromethane layer, now coloured red, was separated out and 5 ml acetone was added into it. This solution was taken in stoppered cylinder and was covered slowly with petroleum ether (40 ml). On standing for a couple of days crystalline product was separated by slow diffusion of the solvents. The product was collected on a sintered bed crucible by suction filtration and washed with dichloromethane and petroleum ether. The product was vacuum dried and analysed. Yield ~ 40%.

Anal. Found: C, 47.22; H, 3.50; Cu, 14.05;  
Mo, 7.52; Cl, 2.52; S, 10.05%.

Calcd for  $\text{Cu}_3\text{C}_{54}\text{H}_{45}\text{As}_3\text{ClMoS}_4$ : C, 47.37; H, 3.29; Cu, 13.93;  
Mo, 7.02; Cl, 2.60; S, 9.36%.

### 3.4b. Preparation of $[\text{Cu}_3\text{As}_3(\text{C}_6\text{H}_5)_9\text{ClWS}_4]$

The complex was synthesised in analogous manner as described for its molybdenum counterpart by using 0.35 g of ammonium tetrathiotungstate in place of ammonium tetrathiomolybdate. The compound thus obtained was filtered in a sintered crucible and washed with dichloromethane and petroleum ether. The complex was vacuum dried and analysed. Yield ~ 45%.

Anal. Found: C, 45.05; H, 3.54; Cu, 13.58;  
Cl, 2.54; S, 9.02%.

Calcd for  $\text{Cu}_3\text{C}_{54}\text{H}_{45}\text{As}_3\text{ClWS}_4$ : C, 44.51; H, 3.09; Cu, 13.08;  
Cl, 2.44; S, 8.79%.

### 3.4c. Preparation of $[\text{Cu}_3\text{As}_3(\text{C}_6\text{H}_5)_9\text{ClMoOS}_3]$

Into a slurry of  $\text{Cs}_2\text{MoOS}_3$  (0.48 g) in DMF, a solution of three equivalents each of freshly prepared  $\text{CuCl}$  (0.30 g) and triphenylarsine (0.92 g) in acetonitrile (50 ml) was added. The resultant mixture was stirred quickly to get most of the insoluble  $\text{Cs}_2\text{MoOS}_3$  into solution. The mixture was filtered off to remove a brown precipitated impurity. Into the filtrate, diethylether was added cautiously to make two distinct layers and kept undisturbed whereby on standing overnight red crystalline compound separated. The crystals were collected in a sintered bed crucible by filtration, washed quickly with acetonitrile and diethylether respectively and vacuum dried. Yield ~52%.

Anal. Found: C, 48.02; H, 3.22; Cu, 14.21;  
Mo, 7.15; Cl, 2.58; S, 7.08%.

Calcd for  $\text{Cu}_3\text{C}_{54}\text{H}_{45}\text{As}_3\text{ClMoOS}_3$ : C, 47.93; H, 3.33; Cu, 14.09;  
Mo, 7.10; Cl, 2.63; S, 7.10%.

### 3.4d. Preparation of $[\text{Cu}_3\text{As}_3(\text{C}_6\text{H}_5)_9\text{ClWOS}_3]$

The compound was synthesised by the method described above for its molybdenum analogue by using 0.56 g of  $\text{Cs}_2\text{WOS}_3$  in place of  $\text{Cs}_2\text{MoOS}_3$ . The compound thus obtained was collected in

### 3.5b. Preparation of $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{WS}_4]$

This compound was synthesised in analogous way as described for its molybdenum analogue replacing 0.18 g of  $(\text{NH}_4)_2\text{WS}_4$  for  $(\text{NH}_4)_2\text{MoS}_4$ . The red brown crystals so obtained were washed with DMSO followed by dichloromethane and diethylether. The compound was vacuum dried and analysed. Yield  $\sim 55\%$ .

Anal. Found: C, 29.20; H, 2.50; N, 8.02;

Cu, 23.95; S, 18.55%.

Calcd for  $\text{Cu}_4\text{C}_{26}\text{H}_{28}\text{N}_6\text{WS}_6$ : C, 29.60; H, 2.66; N, 7.97;

Cu, 24.10; S, 18.22%.

### 3.5c. Preparation of $[\text{Cu}_4(\gamma\text{-pic})_4\text{Cl}_2\text{MoS}_4]$

The complex was synthesised in the same manner as described for  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$ . The cuprous salt used in this case was  $\text{CuCl}$  (0.2 g) instead of  $\text{CuSCN}$ . The compound was filtered by suction, washed with DMSO, dichloromethane followed by diethylether. It was vacuum dried and analysed. Yield  $\sim 50\%$ .

Anal. Found: C, 31.58; H, 3.23; N, 6.24;

Cu, 27.02; Mo, 10.32; S, 14.54;

Cl, 7.92%.

Calcd for  $\text{Cu}_4\text{C}_{24}\text{H}_{28}\text{N}_4\text{Cl}_2\text{MoS}_4$ : C, 31.27; H, 3.04; N, 6.08;  
Cu, 27.58; Mo, 10.42; S, 13.90; Cl, 7.71%.

### 3.5d. Preparation of $[\text{Cu}_4(\gamma\text{-pic})\text{Cl}_2\text{WS}_4]$

The procedure adopted for the synthesis of  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$  was followed. But 0.2 g of CuCl and 0.18 g of  $(\text{NH}_4)_2\text{WS}_4$  were used in place of CuSCN and  $(\text{NH}_4)_2\text{MoS}_4$ , respectively. The compound was filtered through suction, washed with DMSO, followed by dichloromethane and diethylether. The compound was vacuum dried and analysed. Yield ~50%.

Anal. Found: C, 29.04; H, 2.56; N, 5.85;

Cu, 25.65; S, 13.25; Cl, 7.50%.

Calcd for  $\text{Cu}_4\text{C}_{24}\text{H}_{28}\text{N}_4\text{Cl}_2\text{WS}_4$ : C, 28.54; H, 2.78; N, 5.55;

Cu, 25.17; S, 12.69; Cl, 7.03%.

### 3.5e. Preparation of $[\text{Cu}_4(\text{py})_4(\text{SCN})_2\text{MoS}_4]$

The complex was synthesised by the method described for  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$ . The amount of pyridine used was 0.25 ml, instead of  $\gamma$ -picoline. The compound was washed with DMSO followed by dichloromethane and diethylether. It was vacuum dried and analysed. Yield ~52%.

Anal. Found: C, 30.05; H, 1.98; N, 9.56;

Cu, 27.56; Mo, 10.82; S, 21.56%.

Calcd for  $\text{Cu}_4\text{C}_{22}\text{H}_{20}\text{N}_6\text{MoS}_6$ : C, 29.01; H, 2.20; N, 9.23;

Cu, 27.91; Mo, 10.55; S, 21.10%.

### 3.5f. Preparation of $[\text{Cu}_4(\text{py})_4(\text{SCN})_2\text{WS}_4]$

The method of preparation described for  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$  was followed but 0.25 ml of pyridine and 0.18 g of  $(\text{NH}_4)_2\text{WS}_4$  were used in place of  $\gamma$ -picoline and  $(\text{NH}_4)_2\text{MoS}_4$ , respectively. The complex was washed with DMSO followed by dichloromethane and diethylether, respectively, vacuum dried and analysed. Yield  $\sim 60\%$ .

Anal. Found: C, 26.82; H, 2.32; N, 8.56;

Cu, 25.05; S, 19.82%.

Calcd for  $\text{Cu}_4\text{C}_{22}\text{H}_{20}\text{N}_6\text{WS}_6$ : C, 26.45; H, 2.00; N, 8.42;

Cu, 25.45; S, 19.24%.

### 3.5g. Preparation of $[\text{Cu}_4(\text{py})_4\text{Cl}_2\text{MoS}_4]$

The complex was synthesised by the procedure adopted for  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$ , but  $\text{CuCl}$  (0.2 g) was used instead of  $\text{CuSCN}$ . The crystalline compound thus obtained was filtered,

washed with DMSO, dichloromethane and diethylether, respectively and vacuum dried. Yield ~ 54%.

Anal. Found: C, 27.52; H, 2.52; N, 6.55;

Cu, 30.02; Mo, 10.98; S, 15.02; Cl, 8.50%.

Calcd for  $\text{Cu}_4\text{C}_{20}\text{H}_{20}\text{N}_4\text{Cl}_2\text{MoS}_4$ : C, 27.75; H, 2.31; N, 6.47;

Cu, 29.36; Mo, 11.10; S, 14.80; Cl, 8.20%.

### 3.5h. Preparation of $[\text{Cu}_4(\text{py})_4\text{Cl}_2\text{WS}_4]$

The same procedure as adopted for  $[\text{Cu}_4(\gamma\text{-pic})_4(\text{SCN})_2\text{MoS}_4]$  was followed but 0.2 g of CuCl and 0.18 g  $(\text{NH}_4)_2\text{WS}_4$  were used in place of CuSCN and  $(\text{NH}_4)_2\text{MoS}_4$ , respectively. The compound was suction filtered, washed with DMSO followed by dichloromethane and diethylether. It was vacuum dried and analysed. Yield ~ 56%.

Anal. Found: C, 25.56; H, 2.16; N, 5.28;

Cu, 26.85; S, 13.62; Cl, 8.02%.

Calcd for  $\text{Cu}_4\text{C}_{20}\text{H}_{20}\text{N}_4\text{Cl}_2\text{WS}_4$ : C, 25.18; H, 2.10; N, 5.88;

Cu, 26.65; S, 13.43; Cl, 7.45%.



### 3.6 General Properties of the Complexes

The synthesised complexes as described in the preceding pages contain the stoichiometry between tetrathiomolybdate and copper in the ratio, 1:1, 1:2, 1:3 and 1:4, respectively. Among these only the complexes having 1:1 stoichiometry, are anionic and the rest are neutral in nature. The involvement of coligands invariably rests with copper-ligand attachment keeping the tetrathiomolybdate moiety intact which coordinates through sulphur to copper. The possible donor site of the ligands attached to copper which then combine with the tetrathio-metallate moiety are presented in the following table (Table 3.1).

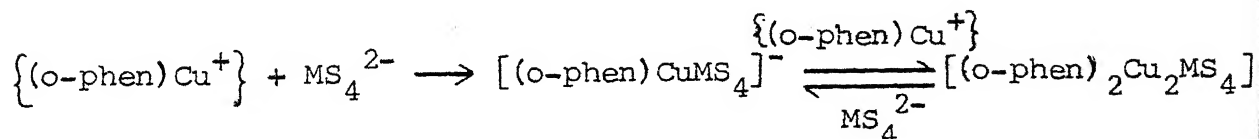
Essentially all these complexes are red in colour; however, there is a trend of the darkening of colour when the ratio of copper is increased. All these complexes contain cuprous ion and thus have closed shell  $3d^{10}$  configuration and the colour is due to the internal transition of tetrathiomolybdate anion. The effect of the coligand attached to  $Cu^+$  has little influence on the low energy band responsible for the colour (vide infra). Other complexes synthesised with oxothiomolybdate are generally orange red to red in colour. The tungsten analogues of these derivatives visually show a deepening in colour on complexation with respect to the free tetrathiotungstate/oxothiotungstate anion.

The anionic complexes in this series are soluble in polar solvents like DMF and DMSO.  $(PPh_4)_2[NCSCuMoS_4]$  is also soluble

TABLE 3.1

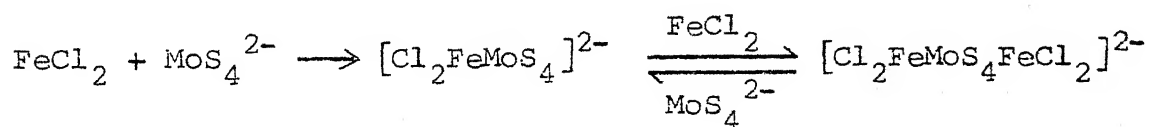
Complex	Ligand	Possible donor site	Cu:MoS <sub>4</sub> ratio	Colour
$[(o\text{-phen})\text{CuMoS}_4]^-$	<i>o</i> -phen	N	1:1	Red
$[\text{NCSCuMoS}_4]^{2-}$	NCS <sup>-</sup>	S	1:1	Red
$[(o\text{-phen})_2\text{Cu}_2\text{MoS}_4]$	<i>o</i> -phen	N	1:3	Red
$[(\text{AsPh}_3)_3\text{Cu}_2\text{MoS}_4]$	AsPh <sub>3</sub>	As	1:2	Red
$[(\text{AsPh}_3)_3\text{Cu}_3\text{ClMoS}_4]$	AsPh <sub>3</sub>	As	1:3	Red
$[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$	$\gamma$ -pic, NCS <sup>-</sup>	N, S	1:4	Violetish red
$[(\gamma\text{-pic})_4\text{Cu}_4\text{Cl}_2\text{MoS}_4]$	$\gamma$ -pic, Cl <sup>-</sup>	N, Cl	1:4	Violetish red

in acetonitrile. The neutral complexes are exceptionally stable in the solid state and they are slightly soluble in DMF and DMSO. In presence of moisture or by washing repeatedly with methanol or ethanol; apparently, hydrolysis takes place which can be seen in their infrared spectra with the appearance of Mo-O vibrational band. However, in the  $\text{H}_2\text{S}$  atmosphere this hydrolysis is sluggish. In the aromatic dimine derivative the attachment of the chelated ligand bound to copper is so strong that it takes several hours to impart the characteristic ferroin colour when, for example,  $[(\text{o-phen})_2\text{Cu}_2\text{WS}_4]$  is treated with  $\text{FeCl}_2$  in DMF or DMSO. Interestingly, a slurry of  $[(\text{o-phen})_2\text{Cu}_2\text{MS}_4]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) in little DMF immediately reacts with an equivalent amount of the respective  $(\text{NH}_4)_2\text{MS}_4$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) to give a clear solution which gives, using appropriate cation, the 1:1 complex  $[(\text{o-phen})\text{CuMS}_4]^-$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ). This anionic complex variety can be directly obtained by using  $\text{Cu}:\text{MS}_4^{2-}$  in 1:1 ratio (vide supra). The interconversion of these 1:1 and 1:2 complexes is schematically summarised below:



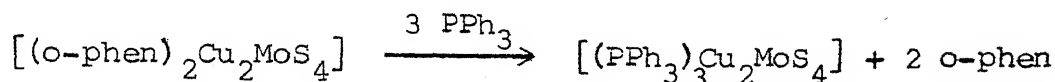
The other species,  $(\text{PPh}_4)_2[\text{NCSCuMoS}_4]$  does not give any 1:2 ( $\text{MoS}_4^{2-}:\text{Cu}^+$ ) complex ion. Several interesting results are recently obtained on the reaction of  $\text{MoS}_4^{2-}$  with  $\text{CuX}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{CN}^-$ ). Thus, when  $\text{CuCN}$  is used,  $\text{MoS}_4^{2-}$  as tetraphenylphosphonium

salt produces the simple dinuclear species,  $(\text{PPh}_4)_2[\text{NCCuMoS}_4]$ , whereas the use of smaller cation like tetramethylammonium ion leads to the isolation to the polymeric species,  $\{(\text{NMe}_4)_2^- \text{NCCu}(\text{MoS}_4)\} \cdot \text{CuCN}$ . Thus, the size of the cation plays a specific role to trap different species present in the reaction mixture. Interestingly,  $(\text{PPh}_4)_2\text{MoS}_4$  reacts smoothly with three equivalents of  $\text{CuCl}$  to give  $(\text{PPh}_4)_2[\text{MoS}_4(\text{CuCl})_3]$ . This monomeric tetranuclear species contains two, four coordinated Cu and one, three coordinated copper using all the four S attached to Mo. In the present case, for the interconversion of dinuclear and trinuclear species, the strongly bonded o-phenanthroline giving  $\{(\text{o-phen})\text{Cu}\}^+$  moiety apparently forces attachment with two S of the  $\text{MoS}_4^{2-}$  achieving thereby four coordination of Cu. The entire process thus can use either 1:1 or 1:2 stoichiometry. A very similar reaction of the above type with biorelevance to the nitrogenase problem has already been observed where the strong Fe-Cl bonds in  $\text{FeCl}_2$  do not cleave in non-aqueous solvent and when allowed to react with  $\text{MoS}_4^{2-}$  species schematically represented below are obtained:



The symmetrical attachment of two  $\{(\text{o-phen})\text{Cu}\}^+$  moiety with one tetrathiometalate leads to the formation of the trinuclear species which contains tetracoordinate copper. However, using monodentate phosphine group as ligand the unsymmetrical

complex is readily formed [21]. Addition of triphenylphosphine into a solution of  $[(o\text{-phen})_2\text{Cu}_2\text{MoS}_4]$  in DMSO leads to the conversion of the symmetrical structure into an unsymmetrical one with the exchange of o-phenanthroline with bulky triphenylphosphine as schematically shown below:



However, the reverse reaction of the above scheme does not take place showing the high tendency of formation of the unsymmetrical species.

Thermally the synthesised complexes are stable upto  $250^\circ\text{C}$ ; however, the neutral complexes slowly start decomposing with the expulsion of the organic ligand. In moist air, on heating, hydrolysis takes place which is evident by the expulsion of  $\text{H}_2\text{S}$ .  $[\text{Cu}_4(\gamma\text{-pic})_4\text{Cl}_2\text{MoS}_4]$  in DMSO reacts with  $\text{AgNO}_3$  to give a precipitate of  $\text{AgCl}$  in the first phase, which slowly turns black in colour with the fading out of the red colour of the DMSO solution. Qualitative analysis of the black precipitate shows the presence of Mo, Cu, Ag, S and  $\text{Cl}^-$  whereas the filtrate shows the presence of Cu besides Ag and  $\text{NO}_3^-$ . Thus, it may be presumed that the chloride attached to copper in the complex can be exchanged with  $\text{NO}_3^-$  of  $\text{AgNO}_3$  which may be unstable and results in the detachment of the Cu-X moiety ( $\text{X} = \text{Cl}^-$ ,  $\text{NO}_3^-$ ) followed by the attachment of the generated  $\text{AgCl}$  in the place of CuX portion.

However, the black residue is not a pure compound as leaching of this with  $\text{Na}_2\text{S}_2\text{O}_3$  solution shows the presence of only Ag in the leached solution without any chloride suggesting the formation of free  $\text{Ag}_2\text{S}$  also in the precipitate.

### 3.7 Possible Relevance of Cu-Mo-S Interaction to Cu-Mo Antagonism

The recent investigations on the interaction of Cu-Mo-S systems reveal that the interaction, in principle, is between copper and tetrathiomolybdate [115]. In vitro generation of thiomolybdate by rumen contents when combined with molybdate and sulphur sources under anaerobic conditions further supports this thiomolybdate hypothesis [123]. Thus, it may be assumed at this stage that copper interacts with tetrathiomolybdate to form stable "Cu-Mo-S complex" which seems to be stable enough to prevent copper to be available for physiological activity. From chemical point of view it would be of prime importance to know about the exactness of the species. Chemically, the interaction between copper and tetrathiomolybdate is known even in aqueous medium where a soluble cupric salt is easily reduced by tetrathiomolybdate to cuprous which gives a polymeric highly insoluble species of the composition  $\text{NH}_4\text{CuMoS}_8$  [8]. However, there are reports that tetrathiomolybdate is rapidly bound to albumin and various other plasma proteins. These thiomolybdate protein

complexes show an increased reactivity toward copper ions. When copper is present in this type of complexes it can not be liberated by TCA precipitation of the proteins [123,124].

Thus, the following points are of special interest to such interactions:

- i) Interaction between free  $\text{Cu}^{n+}$  and  $\text{MoS}_4^{2-}$ .
- ii) Interaction between plasma proteins and  $\text{MoS}_4^{2-}$ .
- iii) Interaction between plasma apo-proteins,  $\text{MoS}_4^{2-}$  and  $\text{Cu}^{n+}$ .

The situation may still be aggravated if one follows the following chemical implications:

(a) The  $\text{S}^{2-}$  formed in the rumen reacts with  $\text{MoO}_4^{2-}$  to produce ultimately  $\text{MoS}_4^{2-}$ .

(b) A competitive reaction between  $\text{Cu}^{n+}$  ion / Cu proteins with  $\text{S}^{2-}$ .

The reaction possibilities in (i) to (iii) is fully dependent on the rate of formation of  $\text{MoS}_4^{2-}$  whereas the formation of  $\text{MoS}_4^{2-}$  as in (a) is going to face the highly competitive reaction between copper and sulphide ion (b).

From the simple solubility product criterion it is evident, at least, chemically, that the  $\text{S}^{2-}$  produced in the rumen is going to interact with copper prior to  $\text{MoO}_4^{2-}$ . Thus,  $\text{CuS}$  once formed may lead  $\text{Cu}^{n+}$  out of metabolic circulation. However, if that be the only situation happening in the rumen, the antagonistic

property of molybdenum remains unresolved. Several experiments on the influence of  $S^{2-}$  concentration alone on the fate of circulated copper do suggest the presence of copper for metabolic activity regardless of the plausible depletion of copper sulphide. This fact prompted thinking that if copper is precipitated as CuS yet, by some interaction this can go into the system. Arguing on this line, one is tempted to think that possibly,  $MoS_4^{2-}$  prevents the resorption of CuS by some chemical interaction. This may be one of the possibilities emerging from simplest possible chemical rationalisation. To check this possibility the following experiments were undertaken.

Reaction between cupric chloride and ammonium heptamolybdate with  $H_2S$

Two equivalents of  $CuCl_2 \cdot 2H_2O$  (2.8 g) and one equivalent of ammonium heptamolybdate (with respect to Mo) (1.8 g) were dissolved in 40 ml aqueous  $NH_3$  (d, 0.7) to get a clear blue solution. Into this  $H_2S$  gas was passed for an hour. Immediately, black precipitate of CuS appeared at the first stage followed by the gradual red colouration of the solution. At this stage all the molybdate had been converted into tetrathiomolybdate (monitored by electronic spectrum of a portion of the filtered solution). The mixture was kept in a glass stoppered flask with stirring overnight whereby most of the black precipitate went into the solution. The solution was quickly filtered under



suction. The filtered solution was then poured into a solution of two equivalents of o-phenanthroline (2.0 g) dissolved in 10 ml DMSO whereby immediately a red precipitate appeared which was filtered under suction, washed twice with ammoniacal  $\text{H}_2\text{S}$  solution followed by acetone and  $\text{CS}_2$ , and finally with diethyl-ether. On analysis and spectral characterisation (vide infra) this was found to be identical with  $[(\text{o-phen})_2\text{Cu}_2\text{MoS}_4]$  (vide supra). It is interesting to mention here that the clear solution obtained by overnight standing, on keeping longer, precipitated the well known polymeric compound  $\text{NH}_4\text{CuMoS}_4$ .

By following similar procedure to obtain a red solution and instead of adding o-phenanthroline, addition of two equivalents of  $\text{CuSCN}$  in 2 ml  $\gamma$ -picoline and 40 ml of DMSO resulted an almost clear solution. Traces of insoluble  $\text{CuSCN}$  went into the solution by magnetically stirring it for about three hours. On long standing (4-5 days) a dark red microcrystalline compound of the composition  $[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$  separated out. It is interesting to note that the above mentioned complexes can be directly synthesised using  $\text{CuSCN}$ ,  $\text{MoS}_4^{2-}$  and appropriate ligand (vide supra).

The above stated experiments do suggest the formation of multinuclear species containing Cu and Mo through the dissolution of  $\text{CuS}$  with the concomitant reduction of  $\text{Cu}^{++}$  to  $\text{Cu}^+$  under the experimental condition.

An analogy of this type of reaction can be drawn from the reaction of  $\text{Fe}^{3+}$  with thiolate ligand. Here too, the stoichiometric dependent polymeric ferric thiolate complex can be solubilised by the use of extra thiolate ligand to give multinuclear cubane type  $\{\text{Fe}_4\text{S}_4\}$  moiety in which partial reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  state takes place [63]. In the present case the situation is not so simple as in the case of polymeric ferric thiolate complex which though insoluble, is very much reactive whereas for CuS the low solubility product and its apparent stability renders it difficult to be incorporated into a reaction so easily. However, the role of  $\text{MoS}_4^{2-}$  is interesting and though we do not have any comparison of this type of bioimportant reaction, at least, in vivo, yet it may be reasonable to assume a similar situation whereby the precipitated CuS may be solubilised by  $\text{MoS}_4^{2-}$  to form a multinuclear species which may finally react with protein rendering copper out of circulation.

Interestingly, the reaction between cupric chloride/tungstate/ $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$  under identical reaction condition as described above does not show any reactivity of  $\text{WS}_4^{2-}$  thus formed, with the in situ precipitated CuS. The corresponding tungstate analogue can be directly synthesised as described earlier ( vide supra ).

The difference in chemical reactivity of these two systems is suggestive enough to say that the involvement of such reaction

with  $\text{MoS}_4^{2-}$  is of complex type wherein the possibility of the reduction of molybdenum present as  $\text{MoS}_4^{2-}$  with  $\text{S}^{2-}$  cannot be ruled out. Recent  $\text{MoS}_4^{2-}$  and  $\text{S}^{2-}$  and/or  $\text{S}^0$  interaction do suggest this type of reduction of molybdenum to formally +5 and +4 oxidation states whereas the thiotungstate system is a sluggish one [125]. This difference between the reactivity of  $\text{MoS}_4^{2-}$  and  $\text{WS}_4^{2-}$  reflects the natural selection of Mo in the biosystem.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Structural Aspects of the Synthesised Complexes

#### Electronic Spectra

Electronic spectra were obtained on a Cary 17D spectrophotometer using matched quartz cells. Solid state spectra were recorded using KBr pellet or the diffused reflectance spectra were recorded by rubbing the compound on white bond paper. The background absorption was minimised using a blank paper. The solvents used were of analytical grade.

### Infrared Spectra

IR spectra of the samples were recorded in the range 4000-200  $\text{cm}^{-1}$  and 4000-400  $\text{cm}^{-1}$  on Perkin Elmer models 580 and 377 infrared grating spectrometers, respectively. Samples were prepared as KBr pellets.

### Raman and Resonance Raman Spectra

Raman and resonance Raman spectra were recorded using a Coderg T800 three-fold monochromator and with one Spex Raman log V two-fold monochromator along with a third monochromator with one RCA C31034 photomultiplier.

As energy source  $\text{Ar}^+$  ion Laser (Coherent CR4; 488.0 nm) or a  $\text{Kr}^+$  ion Laser (Coherent 500 K; 647.1 nm) were used. The resolution with 647.1 nm line for Raman spectral measurement was ca. 5  $\text{cm}^{-1}$  and for resonance Raman spectrum (488.0 nm) ca. 10  $\text{cm}^{-1}$ . Compounds were pressed on KBr disc to get a pressed layer of the compound on KBr planchet and a rotating cell was used to prevent decomposition [126]. The spectrometers were calibrated using Hg lamp or  $\text{CCl}_4$ .

### X-ray Photoelectron Spectroscopy

XPS measurements were carried out using a Vacuum Generators ESCALAB 510 photoelectron spectrometer. The  $\text{Al-K}_\alpha$  X-ray line (1486.6 eV) radiation was used. The samples were measured in

powder form which were fixed by using cellotape. The pressure was kept always lower than  $10^{-8}$  mbar.

The work function of the spectrometer was not determined and binding energies were computed by taking the  $C(1s_{1/2})$  binding energy (285 eV) as standard.

### X-ray Powder Diffractogram Studies

A Philips PW-1050/70 powder diffractometer was used to record the diffractograms.  $Cu-K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) was used as radiation source. Samples were fixed on an aluminium planchet. When less samples were used strong reflection at  $20, 37.9$  and  $44.2^\circ$  appeared which are due to uncovered aluminium.

Raman, resonance Raman and XPS spectra and powder diffractograms were recorded at the University of Bielefeld, West Germany.\*

### 4.1 Electronic Spectra

The electronic spectra of the  $M'-M-S$  complexes show characteristic absorption bands whose positions are roughly comparable to those in the free thiometallates. The  $\nu_1$  absorption of the free thiometallate ions generally splitted on complexation due to the lowering in symmetry. Whenever the central metal ( $M'$ ) contains open d shell configuration, the spectra in this region of ligand internal transition markedly change due to strong metal ligand interactions. Furthermore, the coordination

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\*Courtesy Professor S. Sarkar.

geometry of the central metal, for example in the trimetallic system, causes a considerable perturbation of the electronic structure of the ligand. When iron or cobalt is used as central metal, a band of high intensity in NIR/VIS region appears suggesting strong metal-ligand interaction. Most of the weak d-d transitions may lie under the envelop of the strong ligand to metal and metal to ligand charge transfer. The nature of splitting and other features for a representative class of these complexes have already been presented in Table 1.1.

Complexes containing  $d^{10}$  central atom should give less complex electronic spectra which mainly correspond to ligand internal transitions of the free ligand ions. However, these charge transfer transitions are difficult to assign properly. For the closed shell complex metal ion, the electronic spectra of two species, namely  $[NCCuMoS_4]^{2-}$  and  $[Zn(MoS_4)_2]^{2-}$  have been reported in the literature so far. For both of these complexes complexation results change in the  $\nu_1$  and  $\nu_3$  bands whereas the  $\nu_2$  remains practically unaltered compared to free  $MoS_4^{2-}$  band positions. These results suggested that the  $t_1$  orbital of the  $MS_4^{2-}$  ligand are strongly disturbed than the  $3t_2$ ,  $2e$  and  $4t_2$  m.o.'s on complex formation (Figure 9). M.O. calculations suggest the same trend [21]. This supports the assignments for the three ligand internal transitions as follows:

$$\nu_1 = t_1 \longrightarrow 2e$$

$$\nu_2 = 3t_2 \longrightarrow 2e$$

$$\text{and } \nu_3 = t_1 \longrightarrow 4t_2.$$

The complexes synthesised in the present investigation on the contrary, show a different trend for these transitions. The optical spectra of these complexes are reproduced in Figures 4.1.1 - 4.1.10 and the band positions of these complexes along with those of some compounds existing in literature are tabulated in Table 4.1. These data show that the intensities of the two lowest energy bands are reduced, and the  $\nu_2$  band position is bathochromically shifted. This shift is more pronounced in the trinuclear species. The restricted solubility of these complexes prevented to get any quantitative data for the extinction values of these transitions. However, the solid state spectra of some of the representative species agree with those of the solution spectra regarding band maxima of these complexes. The perturbation of the  $\nu_2$  band of complexes containing open shell central atom reflects  $M' - L$  interaction. The qualitative m.o. scheme as presented in Figure 1.10, uses the following m.o.'s with approximately similar energy:

- (a) non-bonding L m.o.'s with a predominantly 3p(S) character,
- (b) closed or open shell m.o.'s of predominantly 3d( $M'$ ) character, and
- (c) unoccupied  $L^*$  m.o.'s of predominantly 4d(Mo) or 5d(W) character.

It has also been demonstrated by calculations that the m.o. coefficients of the 3d( $M'$ ) type m.o. increases with



TABLE 4.1

Electronic Spectral Data of Synthesised Complexes (in nm)

Compound	Electronic transitions			References
	$\nu_1$	$\nu_2$	$\nu_3$	
$(\text{NH}_4)_2\text{MoS}_4$	467	218	242, 207	127
$(\text{PPh}_4)_2[(\text{o-phen})\text{CuS}_2\text{MoS}_2]$	495	338	260, 242	this work
$(\text{PPh}_4)_2[(\text{NCS})\text{CuS}_2\text{MoS}_2]$	295	338	258, 242	this work
$(\text{NMe}_4)[(\text{NC})\text{CuS}_2\text{MoS}_2]$	272	451, 318	247, 224	21
$[(\text{o-phen})\text{CuS}_2\text{MoS}_2\text{Cu}(\text{o-phen})]$	495	375	258, 242	This work
$[(\text{PPh}_3)_3\text{CuMoS}_4]$	490	370	-	107
$[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$	490	370	245, 210	this work
$[(\text{py})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$	490	370	245, 210	this work
$(\text{NH}_4)_2\text{WS}_4$	386	217	-	21
$(\text{PPh})_4[(\text{o-phen})\text{CuS}_2\text{WS}_2]$	405	300	258, 242	this work
$(\text{PPh}_4)_2[(\text{NCS})\text{CuS}_2\text{WS}_2]$	407	298	266, 260, 242	this work
$[(\text{o-phen})\text{CuS}_2\text{WS}_2\text{Cu}(\text{o-phen})]$	405	340	250, 240	this work
$[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{WS}_4]$	405	335	242	this work
$[(\text{py})_4\text{Cu}_4(\text{SCN})_2\text{WS}_4]$	408	335	255, 252	this work

increasing sulphur content of the thiometallate ligand. Thus a strong  $\pi$  accepting ability due to the presence of low lying unoccupied  $L^*$  orbital is anticipated. Furthermore, the comparable energy of the  $3d(M')$  level & that of the non-bonding m.o.'s of the ligand ( $t_1$  of the free  $MS_4^{2-}$  ion) suggests  $M'-L$  interaction. So, both the types of interactions are possible in principle, and the sequence of m.o.'s in these systems is going to be complicated in nature. Thus, the shift in the position of the  $\nu_2$  band which is more pronounced in the trimetallic system may be due to  $\pi M'-L$  interaction. In this regard it is interesting to note that with the iron thiometallate system a broad absorption band with considerable structure centred around 1000 nm can be seen which has been assigned to  $Fe-L^*$  transition [9].

The reflectance spectra of  $[(PPh_3)_3Cu_2MoS_4]$  shows the appearance of  $\nu_2$  band nearly around 370 nm, which is in close agreement with the data reported herein. Interestingly, for this compound, appearance of a shoulder at ca. 715 nm in its reflectance spectrum has been assigned to a  $d^{10}(Cu) \rightarrow MoS_4^{2-}$  transition [21,128]. The diffuse reflectance spectra of some of the complexes under present investigation do show the appearance of a band around 728 nm (Figure 4.1.11).

Thus, one can assign this transition to  $\pi(Cu) \rightarrow L^*$  type which is liable to disturb the  $\nu_2$  band. The splitting of the  $\nu_1$  band in these complexes were not observed but the broadness

of this band may suggest overlapping of splitted bands.

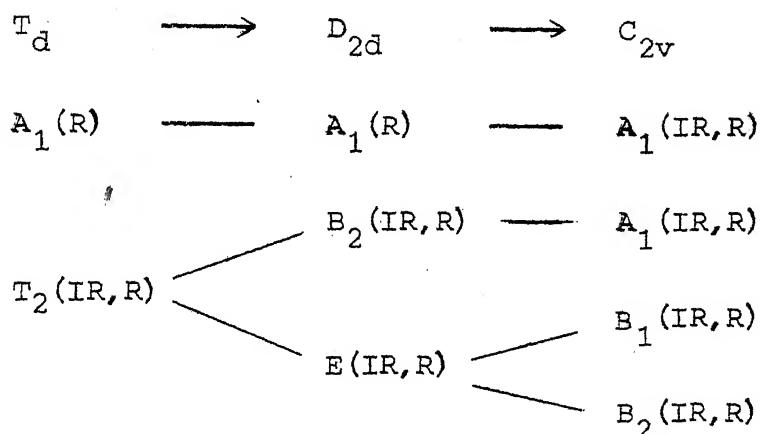
The above stated low energy transition is bound to increase electron density on ligated  $MS_4$  group which can be reflected by the change in the core binding energies of M and S. Furthermore, in the resonance Raman studies, combination of bands for the ligated  $MS_4^{2-}$  chromophore with vibration type  $\nu(Cu-S)$  would lend further support to the above stated electronic interaction between  $Cu^+$  and  $MS_4^{2-}$  in these complexes (vide infra).

#### 4.2 Vibrational Spectroscopy

The structural aspect of the thiometallato complexes can be reasonably determined using infrared spectroscopy followed by assigning the vibrational Raman active modes. As discussed in the introduction chapter, the predicted structure of complexes using this methodology have been substantiated whenever the X-ray structural investigations are made. The mode of ligation of thiometallate anion can be further verified using the corresponding oxothiometallate ligand instead of pure thiometallate one. Invariably, in all these complexes so far known, it is the sulphur which is coordinated to the metal in preference to oxygen in the oxothiometallato species. When binuclear complexes are formed, the thiometallate ligands function as one-fold bidentate ligand leaving a pair of terminal M-S bond leading

thereby to the reduction of local symmetry of the thiometallate group from  $T_d$  to  $C_{2v}$ . When  $MS_4^{2-}$  acts as a two-fold bidentate ligand in trinuclear complexes, the local symmetry of the bridging thiometallato group reduces to  $D_{2d}$ . The correlation of

(M-S) vibrations of  $MS_4$  group in these symmetries are depicted below:



Thus, the  $\nu_1(A_1)$  vibration of the free  $MS_4^{2-}$  ion retains its totally symmetric nature even after coordination and thus this vibration is of the  $\nu_s$  type. However, the asymmetric vibration splitted in two different ways depending on the local symmetry of the coordinated  $MS_4$  group.

In practice, the terminal M-S groups are characterised by one or two vibrational frequencies between  $480-510\text{ cm}^{-1}$  and the bridging (M-S) groups by frequencies between  $430-460\text{ cm}^{-1}$ , respectively. The splitting pattern of the asymmetric mode of vibration in reduced symmetry are not always observed in the

infrared spectra. Representative examples of these type of coordination of some of the structurally characterised species and their infrared spectral data are presented in Table 1.1.

The infrared spectra of the synthesised complexes are presented in Figures 4.2.1 - 4.2.16 and the assignments based on the above stated observations are presented in Tables 4.2.1a and 4.2.1b.

The expected trend observed in dinuclear and trinuclear species are in conformity with the results obtained for the already existing species of the same type. As a check, the Raman spectra of the trinuclear species are recorded and reproduced in Figures 4.2.17 and 4.2.18. The assignments are made following the known Raman data of similar species which are presented in Table 4.2.2. It is interesting to note that in the previously known species of this type with monodentate bulky tertiary phosphine as the coligand, unsymmetrical attachment of the group to copper is observed. The corresponding silver analogue exists in this form as well as in the symmetrical form which is also present in the corresponding dimeric halobridged Cu(I) species (vide supra). The bidentate nature of o-phenanthroline forces formation of the purely symmetric compound,  $[(o\text{-phen})\text{CuS}_2\text{MS}_2\text{Cu}(o\text{-phen})]$ . The high formation tendency and the relative insolubility of these complexes prevented a full structural characterisation by X-ray structure due to the lack of suitable crystal necessary for such studies. Hence, the

TABLE 4.2.1a

Assignment of Mo-S & Mo-O Vibrations in Complexes  
Derived from  $[\text{MoO}_{4-n}\text{S}_n]^{2-}$  Anions (in  $\text{cm}^{-1}$ )

Compound	$\nu(\text{Mo-S})_{\text{br}}$		$\nu(\text{Mo-S})_{\text{term}}$		$\nu(\text{Mo-S})_{\text{term}}$		Reference
	1	2	3	4	4	4	
$(\text{NH}_4)_2\text{MoS}_4$	-	-	472	-	-	-	21
$(\text{PPh}_4)[(\text{o-phen})\text{CuMoS}_4]$	425, 448	448	488, 499	-	-	-	this work
$(\text{PPh}_4)_2[\text{NCSCuMoS}_4]$	440, 450	450	485, 495	-	-	-	this work
$(\text{PPh}_4)_2[\text{NCCuMoS}_4]$	447, 416	416	500, 486	-	-	-	21
$[(\text{o-phen})_2\text{Cu}_2\text{MoS}_4]$	460		-	-	-	-	this work
$[(\text{o-phen})_2\text{Cu}_2\text{MoO}_2\text{S}_2]$	445		-	-	920, 910	-	this work
$[(\text{PPh}_3)_3\text{Cu}_2\text{MoS}_4] \cdot 0.8\text{CH}_2\text{Cl}_2$	465		-	-	-	-	98
$[(\text{AsPh}_3)_3\text{Cu}_2\text{MoS}_4]$	*		-	-	-	-	this work
$[\text{Cu}_3(\text{PPh}_3)_3\text{ClMoS}_4]$	447, 441	441	-	-	-	-	98
$[\text{Cu}_3(\text{AsPh}_3)_3\text{ClMoS}_4]$	*		510	-	-	-	this work
$[\text{Cu}_3(\text{PPh}_3)_3\text{ClMoOS}_3]$	451, 444	444	-	-	923, 908	-	98

contd....

Table 4.2.1a (contd.)

1	2	3	4	5
$[\text{Cu}_3(\text{AsPh}_3)_3\text{ClMoOS}_3]$	*	510	910	this work
$[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$	450	-	-	this work
$[(\gamma\text{-pic})_4\text{Cu}_4\text{Cl}_2\text{MoS}_4]$	450	-	-	this work
$[(\text{py})_4\text{Cu}_4(\text{SCN})_2\text{MoS}_4]$	450	-	-	this work
$[(\text{py})_4\text{Cu}_4\text{Cl}_2\text{MoS}_4]$	450	-	-	this work

\*Masked by  $\text{AsPh}_3$  vibrations.

TABLE 4.2.1b

Assignment of W-S and W-O Vibrations in Complexes  
Derived from  $[\text{WO}_{4-n}\text{S}_n]^{2-}$  Anions (in  $\text{cm}^{-1}$ )

Compound	$\nu$ (W-S) <sub>br</sub>	$\nu$ (W-S) term	$\nu$ (W-O) term	Reference
1	2	3	4	5
(NH <sub>4</sub> ) <sub>2</sub> WS <sub>4</sub>	-	455	-	21
(PPh <sub>4</sub> ) [(o-phen)CuWS <sub>4</sub> ]	448	495	-	this work
(PPh <sub>4</sub> ) <sub>2</sub> [NCSCuWS <sub>4</sub> ]	440, 460	490	-	this work
[(o-phen) <sub>2</sub> Cu <sub>2</sub> WS <sub>4</sub> ]	450	-	-	this work
[(o-phen) <sub>2</sub> Cu <sub>2</sub> WO <sub>2</sub> S <sub>2</sub> ]	440	-	930, 910	this work
[(PPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> WS <sub>4</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	455, 451	-	-	98
[(AsPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> WS <sub>4</sub> ]	*	-	-	this work
[Cu <sub>3</sub> (PPh <sub>3</sub> ) <sub>3</sub> ClWS <sub>4</sub> ]	436, 430	-	-	98
[Cu <sub>3</sub> (AsPh <sub>3</sub> ) <sub>3</sub> ClWS <sub>4</sub> ]	*	515	-	this work
[Cu <sub>3</sub> (PPh <sub>3</sub> ) <sub>3</sub> ClWOS <sub>3</sub> ]	436, 430	-	928, 922	98

128

...contd.



Table 4.2.1b (contd.)

1	2	3	4	5
$[\text{Cu}_3(\text{AsPh}_3)_3\text{ClWOS}_3]$	*	515	920	this work
$[(\gamma\text{-pic})_4\text{Cu}_4(\text{SCN})_2\text{WS}_4]$	432	-	-	this work
$[(\gamma\text{-pic})_4\text{Cu}_4\text{Cl}_2\text{WS}_4]$	432	-	-	this work
$[(\text{py})_4\text{Cu}_4(\text{SCN})_2\text{WS}_4]$	430	-	-	this work
$[(\text{py})_4\text{Cu}_4\text{Cl}_2\text{WS}_4]$	430	-	-	this work

\*Masked by  $\text{AsPh}_3$  vibrations.

TABLE 4.2.2

Raman Spectral Data (in  $\text{cm}^{-1}$ )

Compound	$\nu_s$ (M-S)	$\nu_{as}$ (M-S)	$\nu$ (M'-S)	$\delta$ (MS <sub>2</sub> )	Reference
$[(\text{PPh}_3)_3\text{Cu}_2\text{MoS}_4]$	446	470	267, 303	154	98
$[(\text{PPh}_3)_3\text{Cu}_2\text{WS}_4]$	469	459	257	163	98
$[(\text{PPh}_3)_4\text{Ag}_2\text{MoS}_4]$	462	447	235	167	98
$[(\text{PPh}_3)_4\text{Ag}_2\text{WS}_4]$	441	463	235	162	98
$[(\text{o-phen})_2\text{Cu}_2\text{MoS}_4]$	441	458	258	161	this work
$[(\text{o-phen})_2\text{Cu}_2\text{WS}_4]$	460	450	255	209	this work

resonance Raman Spectroscopy was used to substantiate their structure (vide infra).

The bidentate nature of o-phenanthroline group is important in isolating the symmetrical species as discussed above. However, when monodentate heterocycle nitrogen bases are used, complexes of the stoichiometry  $[L_4Cu_4X_2MS_4]$  ( $L = py, \gamma-pic$ ;  $X = SCN^-, Cl^-$ ;  $M = Mo, W$ ) are obtained.

The appearance of only one  $\nu_s$  (M-S) stretching vibration for these complexes is indicative of the presence of only bridged sulphur in symmetrical fashion. A reasonable proposal for the structure of this variety may be deduced from the genesis of copper-molybdenum-sulphur heteronuclear species from the pure Cu(I) complexes. As described earlier (Chapter I) the trinuclear symmetric or asymmetric Cu-Mo complexes may be thought as derived from the dinuclear halobridged Cu(I) species just by the replacement of the halogen bridge by  $MS_4$  group. Here, this type of substitution retains the copper stoichiometry of the parent dicopper species. Interestingly, the heteronuclear cubane variety containing  $\{XCu_3MS_3\}$  core may be thought as derived from the replacement of three bridged halogen and one copper centre from the pure copper cubane core  $\{Cu_4X_4\}$ , by one  $MS_4$  unit. The difference in the genesis of these two structural variety should be worth noting. The replacement of one copper centre along with the halogen from  $Cu_4X_4$  core, to get the heteronuclear cubane structure, is not unique in the sense that the replacement of  $CuX_2$  core

from the pure binuclear halobridged Cu(I) species with  $MS_4$  group may be thought to produce the dinuclear species. Furthermore, depending on the situation, this displacement may be thought to be either of  $\{LCuX_2\}$  or  $\{L_2CuX_2\}$  moiety. Thus, the pyridine or picoline substituted derivatives comprising  $\{Cu_4MS_4\}$  unit may be thought as the derivative of the chair form of  $Cu_4X_4$  core by the replacement of 4X bridge group by one  $MS_4$  moiety leading thereby to the formation of a sulphur bridged structure. For the present, this proposed structure which is obviously going to be of a new type could not be structurally verified because of the nonavailability of a suitable single crystal. However, X-ray structural characterisation of the species  $[MoS_4(CuCl)_3]^{2-}$  does suggest the genesis of this by the replacement of  $CuX_4$  core from the chair form of  $Cu_4X_4$  unit by  $MoS_4$  group (see Figures 1.7a-1.7d). The stability of the chair form over the cubane variety is known for  $M'_4X_4$  aggregates. The influence of coligand and especially the bulkiness of the tertiary phosphine influence the preferred geometry. When pyridine is used, the chair form is favoured. Hence, when less bulky or smaller ligand is attached to copper the chair variety is preferably formed. The polyheteronuclear aggregates in present study using same type of ligand, thus may have similar structure.

#### Other Ligand Vibration

The coligands used in these newly synthesised complexes contain heterocyclic bases, chloride, thiocyanate and

triphenylarsine. These coligands are attached to copper which can be easily deduced from the characteristic appearance of these ligand vibrations. The identification of Cu-N bond is problematic for the o-phenanthroline complexes as several ligand vibrations also appear in the same frequency region. For the pyridine and picoline derivatives, appearance of a weak band around  $340\text{ cm}^{-1}$  may be due to Cu-N stretching vibration [129-133]. In the picoline derivative, the appearance of a strong band at  $485\text{ cm}^{-1}$  is due to ligand vibration which is absent in the corresponding pyridine compound.

Copper-sulphur stretching vibration can be identified in the Raman spectra of the symmetrical trinuclear species. Assignment in this regard has been made in Table 4.2.2. The modified ligand vibration upon coordination are presented in Table 4.2.3.

For the complexes of the type  $[(\text{AsPh}_3)_3\text{Cu}_3\text{S}_3\text{MXCl}]$  ( $X = \text{O}, \text{S}; M = \text{Mo}, \text{W}$ ) and  $[(\text{AsPh}_3)_3\text{Cu}_3\text{MS}_4]$ , the important M-X stretching vibration can be easily identified. The corresponding M-S stretching vibration in the phosphine analogue is masked by the strong  $\text{PPh}_3$  ligand vibration in this region. However, the bridging M-S vibration in arsine derivatives could not be located due to the presence of strong  $\text{AsPh}_3$  ligand vibrations around  $460\text{ cm}^{-1}$ . But characterisation of all these arsine derivatives can be easily made by comparing the X-ray powder diffractogram of these complexes with those of the corresponding phosphine complexes. The isostructural nature between the arsine complexes

TABLE 4.2.3

## Important Ligand Vibrations Affected on Coordination

Complex	Ligand	Frequency (cm <sup>-1</sup> )	
		Coordinated	Uncoordinated
[PY <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> MoS <sub>4</sub> ]	py	805, 750, 700, 670, 630	405, 605, 650, 700, 747, 886
[PY <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> WS <sub>4</sub> ]	py	800, 750, 690, 665, 620	
[(γ-pic) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> MoS <sub>4</sub> ]	γ-pic	810, 785, 775, 725, 670, 615, 485	405, 480, 604, 668, 728, 749, 872
[(γ-pic) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> WS <sub>4</sub> ]	γ-pic	800, 790, 785, 720, 670, 615, 485	
[(o-phen)CuMoS <sub>4</sub> ] <sup>-</sup>	o-phen	845, 760, 750, 725, 690	885, 853, 622
[(o-phen)CuWS <sub>4</sub> ] <sup>-</sup>	o-phen	845, 760, 750, 725, 690	
[(o-phen) <sub>2</sub> Cu <sub>2</sub> MoS <sub>4</sub> ]	o-phen	865, 845, 840, 720	
[(o-phen) <sub>2</sub> Cu <sub>2</sub> WS <sub>4</sub> ]	o-phen	870, 845, 840, 770, 740, 730	
[(AsPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> MoS <sub>4</sub> ]	AsPh <sub>3</sub>	1560, 1075, 1065, *	1570, 1070, 1060, 1020, 470, 460
[(AsPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> WS <sub>4</sub> ]	AsPh <sub>3</sub>	1562, 1075, 1065, *	
[(AsPh <sub>3</sub> )Cu <sub>3</sub> MoS <sub>4</sub> Cl]	AsPh <sub>3</sub>	1565, 1072, 1068, *	
[(AsPh <sub>3</sub> ) <sub>3</sub> Cu <sub>3</sub> WS <sub>4</sub> Cl]	AsPh <sub>3</sub>	1565, 1075, 1065, *	

\*A band 465 cm<sup>-1</sup> was masked by M-S band of MS<sub>4</sub><sup>2-</sup>.

and the corresponding phosphine complexes could be easily recognised by comparing their diffractograms which are presented in Figures 4.2.19 - 4.2.24.

#### 4.3 Resonance Raman Spectra

Using this technique the influence of the nearest and next nearest neighbours on the vibrations of the ligand chromophore can be investigated [91]. The intensities of bands due to the totally symmetric vibration of the thiomolybdate ligand were strongly enhanced using the 488 nm line of an  $\text{Ar}^+$  laser which falls within the  $\nu_1$  absorption frequency of the internal charge transfer transition of the  $\text{MoS}_4^{2-}$  chromophore. Recently, this technique has been exploited to know the influence of next nearest neighbours whereby a distinction can be made between unsymmetrically and symmetrically substituted  $\text{M}'$  complexes containing trinuclear species. When it is unsymmetrically substituted, the deviation from  $\text{D}_{2d}$  symmetry can clearly be recognised by observing the overtones originated from the combination bands of the type  $n \nu_1(\text{A}) + \nu_1^*(\text{A})$  (assuming  $\text{C}_{2v}$  symmetry for the fragment  $\text{P}_2\text{M}'\text{S}_2\text{MoS}_2\text{M}'\text{P}$ ). These types of combination bands appear as weak feature on the high energy side of the bands of different overtones  $n \nu_1$ . When symmetrically substituted  $\text{M}'$  is present, this type of feature is not expected and only the overtones  $n \nu_1$  are observed.

Compounds containing symmetrically substituted  $M'$  have been subjected to this type of analysis. Amongst these  $[(FeCl_2)_2 MoS_4]^{2-}$  is structurally characterised by X-ray crystallography, whereas for the silver complex  $[(PPh_3)_2 AgS_2 MoS_2 Ag(PPh_3)_2]$ , suitable single crystals for crystal structure determination could not be obtained [91]. The complex  $[(o\text{-phen})CuS_2 MoS_2 Cu(o\text{-phen})]$  under present investigation should show a similar nature of resonance Raman spectra compared to the iron and silver complexes cited above. In Figure 4.3, a typical spectra of these species are reproduced. It is thus evident that all these three complexes are symmetrically substituted on  $M'$  metal and the structural information could be established. A remarkable feature of these spectra is the appearance of combination bands of the type  $n \nu_1 + \nu(M'-S)A_1$  which suggest strong electronic interaction between  $M' (Ag^+, Cu^+)$  and  $MoS_4^{2-}$ . This observation supports the previous discussion regarding electronic interaction between  $d^{10}(Cu)$  and  $MoS_4^{2-}$  centres resulting in the shift of  $\nu_2$  band in the electronic spectra.

#### 4.4 XPS Studies

The determination of binding energy of core electrons makes it possible to deduce the chemical environment of an atom. When similar structural environments are present in a series of complexes, the change in binding energy which reflects the



electron density of an atom may be helpful in assigning the formal oxidation state of an atom. Sometimes complications do arise which may be even helpful in extracting certain information. Thus, an inner shell vacancy, induced by photoionisation, can make a sudden change in the central potential. The relaxation energy of the outer electron, under adiabatic condition, is imparted to the ejected photoelectron. The sudden perturbation of the screening of the remaining electrons may induce a 'shake up' transition involving the excitation of a valence electron to higher unoccupied orbital [134]. This 'shake up' process occurring simultaneously with the core electron photoejection results in satellite lines on the higher binding energy side of the main peak. Selection rules of the sudden approximation suggest that compounds with completely filled d shells, for example, Cu(I), do not have satellite lines [135,136]. Thus, copper when present as cupric does have satellite peaks in the 2p electrons level whereas in Cu(I), these are absent.

In Table 4.4.1 some representative examples of the binding energies of the copper core electrons are presented. The relevant information one might get from these data are following:

(i) In CuCN the metal to ligand back-bonding causes a shift of electron density from filled d orbitals of copper to empty antibonding orbitals of the cyano ligand. The absence of satellite peak can also be seen from its spectrum (Figure 4.4.1). The decrease in the electron density at copper results

in high binding energy of the Cu(2p) electrons.

(ii) The S(2p) binding energy in CuSCN suggests that in the CuSCN there is reduced electron density in the S(2p) level. So is the case with the Cu(I) thiourea complex, where a shift of 1.1 eV of the S(2p) electrons to higher binding energy is noticed for complexed sulphur atom of thiourea, compared to that of the free ligand. This reduction in electron density can be reflected by observing the Cu(2p<sub>3/2</sub>) binding energy in these compounds.

This type of charge flow can be characterised to interpret the actual nature of charge transfer. The influence of the relative binding energy with the oxidation state can be demonstrated easily as has been shown in Figure 1.12. For sulphur also, this is true as it has been shown that unit change in the oxidation state of sulphur results in a shift of about 0.8 eV binding energy [138]. However, a redetermined value for Na<sub>2</sub>S shows the S(2p) binding energy at 162.0 eV [103] contrary to 160.8 eV reported earlier [138]. This is due to the difference in the standardisation procedure but the trend in the different oxidation states are evident.

The binding energies of constituent atoms in the synthesised complexes are presented in Table 4.4.2. The spectra of these species are reproduced in Figures 4.4.2 - 4.4.11. In the anionic complexes the normal trend of the effect of charge present is observed as compared to the neutral species.

TABLE 4.4.2

Binding Energies (ev)

Compound	Cu ( $2p_{3/2}$ )	Mo ( $3p_{3/2}$ )	Mo ( $3d_{5/2}$ )	Mo ( $3d_{3/2}$ )	W ( $4f_{7/2}$ )	W ( $4f_{5/2}$ )	S ( $2p$ )	N ( $1s$ )	S ( $2s$ )
(PPh <sub>4</sub> ) <sub>2</sub> [NCSCuMoS <sub>4</sub> ]	933.5	396.3	230.4	233.4	-	-	162.1	399.1	225.8
(PPh <sub>4</sub> ) [(o-phen)CuMoS <sub>4</sub> ]	933.5	395.9	230.1	233.1	-	-	161.9	399.3	226.2
[(o-phen) <sub>2</sub> Cu <sub>2</sub> MoS <sub>4</sub> ]	933.3	395.6	229.7	232.8	-	-	161.6	399.4	225.8
[( $\gamma$ -pic) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> MoS <sub>4</sub> ]	933.1	396.4	230.4	233.6	-	-	162.9	399.1	227.2
[(py) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> MoS <sub>4</sub> ]	933.0	396.3	230.2	233.8	-	-	162.8	399.1	226.2
(PPh <sub>4</sub> ) <sub>2</sub> [NCSCuWS <sub>4</sub> ]	933.5	-	-	-	34.0	36.2	162.6	399.2	-
(PPh <sub>4</sub> ) [(o-phen)CuWS <sub>4</sub> ]	933.5	-	-	-	33.7	35.9	162.4	399.3	-
[(o-phen) <sub>2</sub> Cu <sub>2</sub> WS <sub>4</sub> ]	933.3	-	-	-	33.4	35.6	162.2	399.7	-
[( $\gamma$ -pic) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> WS <sub>4</sub> ]	933.0	-	-	-	34.0	36.0	162.7	398.7	-
[(py) <sub>4</sub> Cu <sub>4</sub> (SCN) <sub>2</sub> WS <sub>4</sub> ]	933.0	-	-	-	34.1	36.2	162.8	399.0	-

The most interesting fact deduced from the XPS data, is the electron density on the Cu, Mo/W, S atoms in these systems. The Mo( $3p_{3/2}$ ) and Mo( $3d_{3/2}$ ) signals suggest little difference in the electronic charge distribution around molybdenum in its coordinated and uncoordinated form. However, S( $2p$ ) binding energy appears low as compared to that found for uncoordinated  $MoS_4^{2-}$  ion. This low value in binding energy reflects an increase in the electron density on sulphur. The lowest binding energy observed for sulphur in these complexes is with symmetrical trinuclear species,  $[(o\text{-phen})CuS_2Cu(o\text{-phen})]$ ; correspondingly, the increase in the binding energy for Cu( $2p_{3/2}$ ) in this complex compared to that in the free CuSCN is suggestive of a reduction in electron density at the copper in this complex. These two observations together substantiate an electron flow from copper to sulphur, of the  $MoS_4^{2-}$  group. This trend is in accord with the results obtained through resonance Raman and electronic spectral studies.

## CHAPTER V

### BIORELEVANCE OF THE PRESENT WORK

Nutritional significance of trace elements in biological systems is gaining momentum exponentially. Though it is rare for an interaction between trace elements to draw more attention than do the trace elements themselves, but it is true for the interaction between copper and molybdenum.

The interaction of copper is possible with many essential trace elements inside the organism which is represented schematically in Figure 5.1. These interactions may result in the stimulation or antagonism of each other. Since the effect of excess molybdenum results in the depletion of copper for metabolic purposes, the interaction between copper and

molybdenum is referred to as 'Cu-Mo Antagonism' [139]. The first report of such an interaction came in 1938 when the cattle grazing pastures on molybdenum rich soil developed acute diarrhea and debilitation [140]. The disease referred to as 'teart' could be cured by spraying the pastures or watering the animals with  $\text{CuSO}_4$  solution. Evidently, the deficiency of copper induced by excess of molybdenum was supposed to be the reason for the disease.

From various experiments it was concluded that high molybdenum and sulphate intake disturb the metabolic efficiency of copper utilisation and induce copper deficiency [111]. Thus, 'Cu-Mo antagonism' may be viewed as an interaction between Cu, Mo and S. Interestingly, there is difference in the mode of interaction between these elements in monogastrics and ruminants which is attributed to the difference in their digestive systems. In ruminants, the microbial activity in the forestomachs (rumen) is responsible for production of  $\text{S}^{2-}$  by the reduction of sulphate as well as from the degradation of sulphur containing amino acids. Moreover, since molybdenum inhibits sulphite oxidase, the accumulation of  $\text{S}^{2-}$  may take place in the liver also, of the ruminants. In monogastrics, sulphate inhibits the absorption of molybdate and so the accumulation of molybdenum in liver is less. Hence, ruminants are more affected than monogastrics by such interaction. It is notable that in ruminants, the antagonism of copper metabolism

by molybdenum is potentiated by dietary sulphur, occurs at low molybdenum concentration and results in depletion of tissue copper whereas in monogastrics it is alleviated by sulphur, occurs at high molybdenum concentration and results in tissue copper accretion.

Now it is fairly established at least in vitro, that thio-molybdate which is formed by interaction between  $\text{MoO}_4^{2-}$  and  $\text{S}^{2-}$ , is the strongest antagonist of copper [141,142]. Mills in 1979 has proposed a comprehensive account of these interactions and has summarised his observations in the form of a flow-sheet represented in Figure 5.2, and has concluded that molybdenum interferes with copper metabolism both before and after resorption [114]. A Cu-thiomolybdate-protein complex of poor physiological availability is suggested to be responsible for the depletion of copper. Hence, the synthesis of copper-thiomolybdate-protein complex may shed some light on the chemical implication of this phenomenon and may contribute quantitatively towards rationalising the difference in its modus operandi in ruminants and monogastrics.

Although the polymeric compound,  $\text{NH}_4\text{CuMoS}_4$ , may be taken to be an example of a complex which is obtained by interaction of copper ions with  $(\text{NH}_4)_2\text{MoS}_4$  (vide supra), it does not take into account the protein interaction. Synthesis of some  $\text{Cu-MoS}_4^{2-}$  complexes flanked by P-donor ligands have been reported (vide supra) but again the presence of P-donor ligands

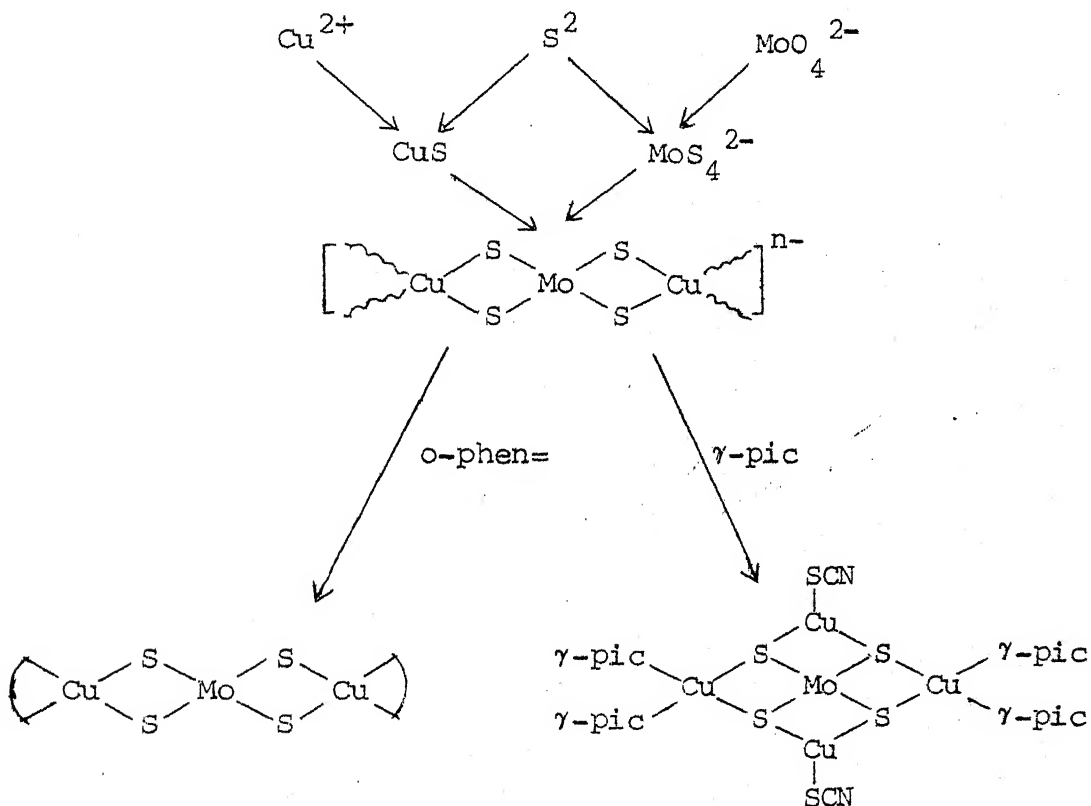
is questionable either in monogastrics or ruminants. Thus, complexes of  $\text{Cu-MoS}_4^{2-}$  flanked by N-donor ligands may be close to the realistic situation because N is a potential donor site in most proteins. Hence, the complexes described in the thesis may be considered to be the closest models of Cu-Mo interaction.

Furthermore, in earlier attempts to rationalise Cu-Mo interaction, the interaction between  $\text{Cu}^{n+}$  ion and  $\text{S}^{2-}$  before the interaction of  $\text{Cu}^{n+}$  with  $\text{MoS}_4^{2-}$  has been ignored [115, 143-145]. But there is no reason why  $\text{Cu}^{n+}$  would not react with  $\text{S}^{2-}$  when it is present in situ to interact with  $\text{MoO}_4^{2-}$ . In fact, even in a competitive reaction between  $\text{Cu}^{n+}$  and  $\text{MoO}_4^{2-}$  to interact with  $\text{S}^{2-}$ , it is CuS which would be formed first in preference to  $\text{MoS}_4^{2-}$  according to the concept of solubility product. Hence, the possibility of the formation of CuS and  $\text{MoS}_4^{2-}$  separately in the rumen in an earlier phase of interaction may not be ignored.

In view of these, the experiment described in Chapter III demonstrating the solubility of CuS in presence of  $\text{MoS}_4^{2-}$  in aqueous medium with  $\text{S}^{2-}$  is of immense importance. And the flow-sheet of Mills which proposes resorption of  $\text{MoS}_4^{2-}$  in the form of  $\text{MoS}_4^{2-}$  protein complex followed by its interaction with copper in the tissue may not be the only pathway for the resorption process. The resorption of CuS and  $\text{MoS}_4^{2-}$  together, and the subsequent isolation (vide supra) of o-phenanthroline and  $\gamma$ -picoline complexes from the aqueous solution (containing CuS and  $\text{MoS}_4^{2-}$ ), is suggestive enough to hypothesise that copper-



thiomolybdate N-donor complexes can be formed by a direct resorption process if N-donors can be taken as representative of the protein unit. These reactions may be schematically represented as follows:



A very interesting observation that such type of reaction, namely resorption of  $\text{CuS}$ , and hence, the isolation of multimetal complexes does not take place with  $\text{WS}_4^{2-}$  in aqueous solution, reflects the nature's choice for molybdenum over tungsten for biological incorporation (vide supra). These observations are consistent with a recent in vivo experiment by Mills and

coworkers where the behaviour of molybdenum and tungsten are different when  $\text{MoO}_4^{2-}/\text{WO}_4^{2-}$  were allowed to interact with  $\text{S}^{2-}$  (generated intraruminally from  $\text{SO}_4^{2-}$ ) [146].

Based on the above observations a scheme represented in figure 5.3 is proposed for Cu-Mo interaction responsible for clinical deficiency of copper in physiological conditions.

Had the protein-Cu-MoS<sub>4</sub> complex been synthesised incorporating imidazole, histidine, cysteine and other N, S, O donor amino acids, one can envisage that the model would have been more realistic and comprehensive. Attempts to synthesise complexes using these ligands resulted in species with varied stoichiometry. However, tailor-made metal clusters using desirable units are difficult to synthesise. The difficulty is augmented by the presence of different heterometal species in the solution and hence a proper choice of counterions, solvent systems and an inherent methodology is necessary.

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